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Published by : NODIA
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ISC EXAMINATION PAPER 2026

CHEMISTRY

CLASS XII

Time: 3 Hours **Max. Marks: 70**

General Instructions:

1. You are allowed an additional 15 minutes for only reading the question paper.
2. You must NOT start writing during the reading time.
3. This question paper is divided into four sections and has twenty one questions in all.
4. Answer all questions.
5. Section A has fourteen subparts. Each question carries 1 mark.
6. While attempting Multiple Choice Questions in Section A, you are required to write only ONE option as the answer.
7. Section B has ten questions. Each question carries 2 marks.
8. Section C has seven questions. Each question carries 3 marks.
9. Section D has three questions. Each question carries 5 marks.
10. Internal choices have been provided in one question each in Sections B, C and D.
11. The intended marks for questions are given in brackets [ ].
12. All working, including rough work, should be done on the same sheet as, and adjacent to the rest of the answer.
13. Balanced equations must be given wherever possible and diagrams where they are helpful.
14. When solving numerical problems, all essential workings must be shown.
15. In working out problems, use the following data:
    Gas constant R = 1.987 cal K^{-1} mol^{-1} = 8.314 J K^{-1} mol^{-1} = 0.0821 dm^3 atm K^{-1} mol^{-1}
    1 L atm = 1 dm^3 atm = 101.3 J, 1 faraday = 96,500 coulombs
    Avogadro's number = 6.023×10^{23}

SECTION A 14 MARKS

QUESTION 1.

(A) Fill in the blanks by choosing the appropriate word(s) from those given in the brackets: [4 × 1]
[first, alc. AgCN, primary, decrease, third, increase, zero, Lucas, alc. KCN, KOH, no change, two, Tollen's, AgOH, tertiary]

(i) A mixture of anhydrous $ZnCl_2$ and conc. HCl is called _____ reagent which shows maximum reactivity with _____ alcohol.

Ans :

Lucas, tertiary

(ii) Methyl chloride on treatment with _____ forms methyl cyanide, whereas on treatment with _____ it forms methyl isocyanide.

Ans :

alc. KCN, alc. AgCN

(iii) The hydrolysis of ethyl acetate in acidic medium is a pseudo _____ order reaction. However, the molecularity of the reaction is _____.

Ans :

first, two

(iv) Dissociation of solute particles leads to a/an _____ in the magnitude of a colligative property and a/an _____ in the value of the observed molecular mass.

Ans :

increase, decrease

(B) Select and write the correct alternative from the choices given below. [7 × 1]

(i) Which one of the following is a tetrahedral complex as well as diamagnetic in nature?
(a) $[Ni(CN)_4]^{2-}$
(b) $[NiCl_4]^{2-}$
(c) $[Cu(NH_3)_4]^{2+}$
(d) $[Ni(CO)_4]$

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Ans :

(d) $[Ni(CO)_4]$
In this complex, nickel is in the 0 oxidation state (since CO is neutral), giving the configuration $3d^{10}\ 4s^0$. CO is a strong-field ligand, but here all 3d electrons are already paired. The 4s and 4p orbitals undergo sp^3 hybridization, giving a tetrahedral geometry. Since all electrons are paired, the complex is diamagnetic. Hence, $[Ni(CO)_4]$ is both tetrahedral and diamagnetic.

(ii) When H_2S gas is passed through acidified $K_2Cr_2O_7$ solution, the colour of the solution changes to:
(a) green (b) orange
(c) black (d) red

Ans :

(a) green
Reaction of $K_2Cr_2O_7$ with H_2S gas is given by
$Cr_2O_7^{2-} + 3H_2S + 8H^+ \rightarrow 2Cr^{3+} + 3S + 7H_2O$
Dichromate ion is orange in colour. The solution changes from orange to green due to the formation of Cr^{3+} ions.

(iii) Identify the end product [C] in the following sequence of chemical reaction:
$CH \equiv CH \xrightarrow{dil.H_2SO_4/HgSO_4} [A] \xrightarrow{[O]} [B] \xrightarrow{PCl_5} [C]$
(a) Acetic anhydride
(b) Acetic acid
(c) Acetyl chloride
(d) Ethyl chloride

Ans :

(c) Acetyl chloride
The complete reaction is shown below:

$$CH \equiv CH \xrightarrow{dil.H_2SO_4/HgSO_4} CH_3CHO \xrightarrow{[O]} CH_3COOH \xrightarrow{PCl_5} CH_3COCl$$

Hence, compound C is acetyl chloride.

(iv) Rohit is studying the iodoform reaction by using the following compounds:
(P) CH_3OH
(Q) CH_3CHO
(R) CH_3COCH_3
(S) $CH_3CH_2–CO–CH_2–CH_3$
Which of the following combinations will give an iodoform test when the compounds are heated separately with iodine and aqueous NaOH?
(a) Only (P) and (Q)
(b) Only (Q) and (R)
(c) Only (P) and (S)
(d) Only (Q) and (S)

Ans :

(b) Only (Q) and (R)
Acetaldehyde (CH_3CHO) and acetone (CH_3COCH_3) both contain the $CH_3CO–$ group required for the iodoform test. When heated with I_3 and aqueous NaOH, this group is converted into iodoform (CHI_3), a yellow precipitate. Hence, only (Q) and (R) give a positive iodoform test.

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(v) Which one of the following nitrogen bases is absent in RNA?
(a) Adenine
(b) Guanine
(c) Uracil
(d) Thymine

Ans :

(d) Thymine
Nucleic acids contain two types of nitrogenous bases: purines (adenine and guanine) and pyrimidines (cytosine, thymine, and uracil). Both DNA and RNA share three common bases — adenine, guanine, and cytosine — but differ in the fourth. DNA contains thymine, whereas RNA contains uracil in its place. Thus, the four bases in RNA are adenine, guanine, cytosine, and uracil. Therefore, thymine is absent in RNA, as it is replaced by uracil, which differs from thymine only by the absence of a methyl group.

(vi) Given below are two statements marked Assertion and Reason. Read the two statements carefully and select the correct option.
Assertion : Phenols are more acidic than aliphatic alcohols.
Reason : Phenoxide ion is stabilised by resonance but alkoxide ion is not stabilised by resonance.
(a) Both Assertion and Reason are true and Reason is the correct explanation for Assertion.
(b) Both Assertion and Reason are true but Reason is not the correct explanation for Assertion.
(c) Assertion is true and Reason is false.
(d) Both Assertion and Reason are false.

Ans :

(a) Both Assertion and Reason are true and Reason is the correct explanation for Assertion.
Phenol forms phenoxide ions, and aliphatic alcohols form alkoxide ions. The negative charge in phenoxide ion is delocalised over the benzene ring at ortho and para positions through resonance, which stabilises it. Since phenoxide ion is more resonance-stabilised, there is no resonance in

alkoxide ion (negative charge remains localised on oxygen only), phenoxide ion is more stable than alkoxide ion. Hence, phenol is more acidic than aliphatic alcohols.

(vii) Given below are two statements marked Assertion and Reason. Read the two statements carefully and select the correct option.

Assertion : The depression of freezing point of 0.1 molal aqueous solution of $MgCl_2$ is less than that of 0.1 molal aqueous solution of NaCl.

Reason : The number of particles furnished by 0.1 molal $MgCl_2$ is less than that of 0.1 molal NaCl.

(a) Both Assertion and Reason are true and Reason is the correct explanation for Assertion.
(b) Both Assertion and Reason are true but Reason is not the correct explanation for Assertion.
(c) Assertion is true and Reason is false.
(d) Both Assertion and Reason are false.

Ans :

(d) Both Assertion and Reason are false.
0.1 m NaCl → dissociates as:
$NaCl \rightarrow Na^+ + Cl^-$; $i \approx 2$
0.1 m $MgCl_2$ → dissociates as:
$MgCl_2 \rightarrow Mg^{2+} + 2Cl^-$; $i \approx 3$

Since, $\Delta T_f = i.K_f.m$

Hence, the depression in freezing point is higher in a 0.1 molal aqueous solution of $MgCl_2$ than in a 0.1 molal aqueous solution of NaCl.

(C) Read the information given below and answer the questions that follow.

Kohlrausch observed an interesting pattern between the values of molar conductance at infinite dilution ($\Lambda°m$) for strong electrolytes. It was observed that different pairs of electrolytes having a common cation or anion had almost same difference of $\Lambda°m$.

On the basis of his observation, he postulated a law known as Kohlrausch's Law of Independent Migration of ions. [3 × 1]

The values of molar conductivities at infinite dilution for some cations and anions are as follows:

Ion	**$\Lambda°m$ (S cm² mol⁻¹)]**
Ba^{2+}	127.2
Cl^-	76.3
Ca^{2+}	119.0
SO_4^{2-}	160.0

(i) State the Kohlrausch's Law of Independent Migration of ions.

Ans :

The law states that the molar conductivity at infinite dilution, each ion contributes independently to the total molar conductivity of an electrolyte, irrespective of the nature of the other ion present.

Mathematically, for an electrolyte:

$$\Lambda°_m = \upsilon_+\lambda°_+ + \upsilon_-\lambda°_-$$

(ii) Calculate the molar conductance at infinite dilution $\Lambda°m$ for $BaCl_2$.

Ans :

For $BaCl_2$, $BaCl_2 \rightarrow Ba^{2+} + 2Cl^-$
According to the Kohlrausch's Law

$$\Lambda°_m(BaCl_2) = \lambda^{\infty}_{Ba^{2+}} + 2\lambda^{\infty}_{Cl^-}$$
$$\Lambda°_m(BaCl_2) = 127.2 + 2(76.3)$$
$$= 127.2 + 152.6$$
$$= 279.8 \text{ S cm}^2 \text{ mol}^{-1}$$

(iii) Arrange the values of $\Lambda°m$ for $CaSO_4$ and $BaCl_2$ in increasing order.

Ans :

Now calculate for $CaSO_4$:
$CaSO_4 \rightarrow Ca^{2+} + SO_4^{2-}$

$$\Lambda°_m(CaSO_4) = 119.0 + 160.0$$
$$= 279.0 \text{ S cm}^2 \text{ mol}^{-1}$$

Hence, increasing order of $\Lambda°_m$: $CaSO_4$ (279.0) < $BaCl_2$ (279.8)

SECTION B 20 MARKS

QUESTION 2.

A reaction is of first order with respect to reactant [A] and second order with regard to reactant [B].

What is the effect on rate of reaction when:

(i) concentration of only [B] is increased three times?

(ii) concentration of both [A] and [B] is doubled?

Ans :

For a reaction that is first order in [A] and second order in [B], the rate law is:

$$R = k[A]^1[B]^2$$

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(i) When the concentration of only [B] is increased three times, while [A] remains unchanged.

$$B' = [3B]$$

$$R' = k[A]^1[3B]^2$$

$$= (3)^2.k[A]^1[B]^2 = 9R$$

Hence, rate increases nine times.

(ii) Concentration of both [A] and [B] is doubled; Let the new concentrations be 2[A] and 2[B].

$$A' = [2A],\ B' = [2B]$$

$$R' = k[2A]^1[2B]^2$$

$$= (2)^3.k[A]^1[B]^2$$

$$= 8R$$

The rate of reaction becomes 8 times the original rate.

QUESTION 3.

(i) 0.680 g of a compound is dissolved in 15.0 g of benzene and the freezing point of solution is lowered by 1.44°C.
Calculate the experimental molecular mass of the compound.
(K_f for benzene = 5.12 K kg mol^{-1})

(ii) If the theoretical molecular mass of the compound referred to above is 80.5 g mol^{-1}, suggest whether it is undergoing association or dissociation.

Ans :

(i) Given, $\Delta T_f = 1.44$ K

$$K_f = 5.12 \text{ K kg mol}^{-1}$$

$$m = 1.44 \text{ K} / 5.12 \text{ K kg mol}^{-1}$$

$$= 0.28125 \text{ kg mol}^{-1}$$

$$\Delta T_f = K_f \times m$$

$$= K_f \times \frac{\omega_2 \times 1000}{M_2 \times \omega_1}$$

$$m = \frac{w_B \times 1000}{w_A \times M_B}$$

$$0.28125 = \frac{0.680 \times 1000}{15.0 \times M_B}$$

$$M_B = 161.2 \text{ g mol}^{-1}$$

(ii) Theoretical molar mass = 80.5 g mol^{-1}
Experimental molar mass = 161.2 g mol^{-1}

$$i = \frac{\text{Theoretical Molar Mass}}{\text{Experimental Molar Mass}}$$

$$= 80.5 / 161.2 \approx 0.5$$

Since $i < 1$, the compound is undergoing association.

QUESTION 4.

Write the IUPAC names of the following complex compounds:

(i) $[Pt(NH_3)_4Cl_2]SO_4$

(ii) $K_2[Ni(CN)_4]$

Ans :

(i) Tetraamminedichloridoplatinum (IV) sulphate.

(ii) Potassium tetracyanonickelate(II) or Potassium tetracyanidonickelate(II)

QUESTION 5.

Write chemical equations to convert each of the following:

(i) Methyl magnesium bromide to propan-2-ol

(ii) Phenol to benzene

Ans :

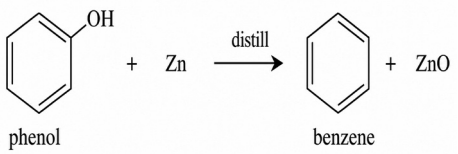
(i) Methyl magnesium bromide to propan-2-ol
Grignard reagent reacts with acetaldehyde (ethanal) followed by hydrolysis.
Step 1: Formation of addition product

$CH_3MgBr + CH_3CHO \rightarrow CH_3CH(OMgBr)CH_3$

Step 2: Hydrolysis

$CH_3CH(OMgBr)CH_3 \xrightarrow{H_3O^+} CH_3CH(OH)CH_3 + Mg(OH)Br$

(ii) phenol to benzene



QUESTION 6.

Calculate the value of ΔG° for the following cell at 25°C.

$Zn(s)/Zn^{2+}(1M) \parallel Sn^{2+}(1M)/Sn(s)$

Given $E^0_{Zn^{2+}/Zn} = -0.76$ V

$E^0_{Sn^{2+}/Sn} = -0.14$V

1 faraday = 96,500 coulombs

Ans :

For the given cell, $Zn(s)|Zn^{2+}(1M)||Sn^{2+}(1M)|Sn(s)$

$$E^\circ_{Zn^{2+}/Zn} = -0.76 \text{ V}$$

$$E^\circ_{Sn^{2+}/Sn} = -0.14 \text{ V}$$

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$$E°\text{cell} = E°_{\text{cathode}} - E°_{\text{anode}}$$
$$= E°_{Sn^{2+}} - E°_{Zn^{2+}}$$
$$= -0.14 - (-0.76) = 0.62 \text{ V}$$

Cell equation:

$Zn(s) + Sn^{2+}(aq) \rightarrow Zn^{2+}(aq) + Sn(s)$;

$$n = 2$$

Hence, $\Delta G° = -nFE°_{\text{cell}}$

$$= -2 \times 96{,}500 \times 0.62$$
$$= -119{,}660 \text{ J}$$
$$\Delta G° \approx -1.20 \times 10^5 \text{ J}$$
$$\Delta G° \approx -120 \text{ kJ mol}^{-1}$$

QUESTION 7.

Write chemical reactions for the following named organic reactions:

(i) Diazotisation reaction

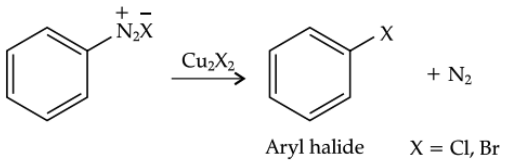
(ii) Sandmeyer's reaction

Ans :

(i)

$$\underset{\text{Aniline}}{C_6H_5-NH_2} \xrightarrow[273-278K]{NaNO_2+2HCl} \underset{\text{Benzenediazonium chloride}}{C_6H_5-N_2^+Cl^-} + NaCl + 2H_2O$$

(ii)



QUESTION 8.

A first order reaction is 40% complete in 20 minutes.

Calculate the time required for 90% completion of the same reaction.

Ans :

As we know that , for first order:

$$k = \left(\frac{2.303}{t}\right) \times \log\left(\frac{[A]_0}{[A]_t}\right)$$

If 40% is complete, 60% remains in 20 minutes:

$$k = \left(\frac{2.303}{20}\right) \times \log\left(\frac{100}{60}\right)$$
$$= \left(\frac{2.303}{20}\right) \times \log\left(\frac{5}{3}\right)$$
$$= \left(\frac{2.303}{20}\right) \times 0.2218 = 0.02555 \text{ min}^{-1}$$

For 90% completion (10% remains):

$$t = \left(\frac{2.303}{k}\right) \times \log\left(\frac{100}{10}\right)$$
$$= \left(\frac{2.303}{0.02555}\right) \times \log(10)$$
$$= \left(\frac{2.303}{0.02555}\right) \times 1$$
$$= 90.1 \text{ minutes}$$

Time required for 90% completion ≈ 90.1 minutes.

QUESTION 9.

(i) Write chemical tests to distinguish between the following pairs of compounds:

(a) Acetaldehyde and acetone

(b) Acetic acid and benzaldehyde

Ans :

(a) Tollen's test (silver mirror test)

Acetaldehyde + Ammonical silver nitrate → Silver mirror

$CH_3CHO + 2[Ag(NH_3)_2]^+ + 2OH^- \rightarrow CH_3COO^- + 2Ag\downarrow + 4NH_3 + H_2O$

Acetone + Ammonical silver nitrate → no reaction

(b) Acetic acid and benzaldehyde

Test – Sodium bicarbonate test

Acetic acid (CH_3COOH) + $NaHCO_3$ → brisk effervescence

Benzaldehyde + $NaHCO_3$ → No effervescence

or

(ii) An organic compound [A] having molecular formula C_3H_8O gives turbidity with Lucas reagent within five minutes of mixing. On heating compound [A] with Cu at 573K, compound [B] is formed. Compound [B] does not reduce Fehling's solution but when heated with iodine and sodium hydroxide, it gives a yellow precipitate of compound [C]. Identify the compounds [A], [B] and [C].

Write the chemical reaction for the conversion of compound [B] to compound [C].

Ans :

Compound [A] with molecular formula C_3H_8O gives turbidity after 5 minutes with Lucas reagent. Hence, Compound [A] must be Isopropyl alcohol (secondary alcohol). Heating compound [A] propan-2-ol with Cu at 573K, compound [B] acetone is formed. Compound [B], acetone being a ketone, does not reduce Fehling's solution, but reacts with iodine and sodium hydroxide forming a yellow precipitate. This confirms Compound [B]

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is methyl ketone. And the precipitate formed on reaction is Iodoform (CHI_3).

Compound [A]	Propan-2-ol (Isopropyl alcohol)
Compound [B]	Propanone (Acetone)
Compound [C]	Iodoform (CHI_3)

Chemical reaction:

$CH_3–CHOH–CH_3 \xrightarrow[573K]{Cu} CH–CO–CH_3$

$CH_3COCH_3 + 3I_2 + 4NaOH \rightarrow CHI_3(\downarrow) + CH_3COONa + 3NaI + 3H_2O$

QUESTION 10.

(i) Why is the first ionisation enthalpy of chromium less than that of zinc?
(Atomic Number of Cr = 24 and Zn = 30)

(ii) Why does pink colour of aqueous $KMnO_4$ solution disappear when warmed with oxalic acid solution in acidic medium?

Ans :

(i) Cr (Z = 24) → [Ar] $3d^5\ 4s^1$
Zn (Z = 30) → [Ar] $3d^{10}\ 4s^2$
Chromium attains a stable half-filled $3d^5$ configuration after losing one electron, so removal of the first electron requires comparatively less energy.
In contrast, zinc has a filled $3d^{10}\ 4s^2$ configuration, which is very stable. Removal of one electron from zinc disturbs this stable configuration and requires more energy. Hence, the first ionisation enthalpy of chromium is lower than that of zinc.

(ii) Reaction of aqueous $KMnO_4$ with oxalic acid in acidic medium:
$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$
$KMnO_4$ acts as a strong oxidising agent. In acidic solution, permanganate ions (MnO_4^-), which are pink, are reduced to Mn^{2+} ions, which are nearly colourless.

QUESTION 11.

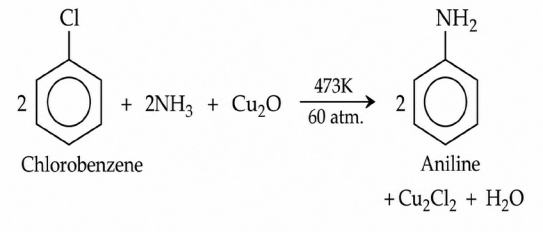
Write chemical equations to convert each of the following:

(i) Chlorobenzene to aniline

(ii) Iodoform to acetylene

Ans :

(i) Chlorobenzene to aniline



(ii) Iodoform to acetylene

$\underset{\text{Iodoform}}{2CHI_3} + 6Ag + \xrightarrow{\text{Heat}} \underset{\substack{\text{Ethyne}\\(\text{acetylene})}}{H-C\equiv C-H} + 6AgI$

SECTION C 21 MARKS

QUESTION 12.

Write chemical equations to convert each of the following:

(i) Methanol to ethanol

(ii) Benzene diazonium chloride to phenol

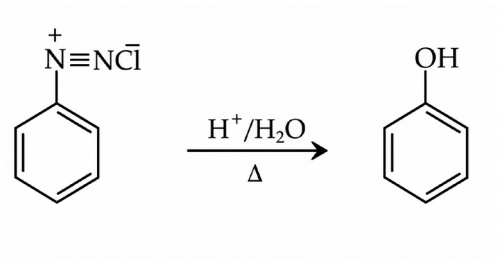
(iii) Sodium ethoxide to ethoxyethane

Ans :

(i)

$CH_3OH + HBr \rightarrow CH_3Br \xrightarrow[\text{dry ether}]{Mg} CH_3MgBr$
$+ HCHO \rightarrow CH_3CH_2OMgBr + H_2O$
$\rightarrow CH_3CH_2OH + Mg(OH)Br$

(ii)



(iii) Sodium ethoxide to ethoxyethane
$C_2H_5ONa + C_2H_5Br \rightarrow C_2H_5–O–C_2H_5 + NaBr$

QUESTION 13.

(i) Complete and balance the following reactions:
(a) $K_2Cr_2O_7 + H_2SO_4 + KI \rightarrow$ ___ + ___ + ___ + ___
(b) $KMnO_4 + H_2SO_4 + FeSO_4 \rightarrow$ ___ + ___ + ___ + ___

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(ii) Which ion, Co^{2+} or Zn^{2+}, is attracted to a magnetic field? Give reasons.
(Atomic Number of Co = 27 and Zn = 30)

Ans :

(i) (a) $K_2Cr_2O_7 + 7H_2SO_4 + 6KI \rightarrow Cr_2(SO_4)_3 + 4K_2SO_4 + 3I_2 + 7H_2O$

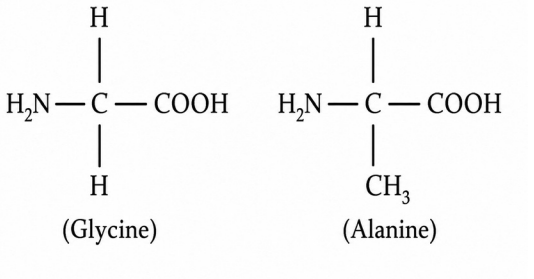
(b) $2KMnO_4 + 8H_2SO_4 + 10FeSO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$

(ii) Co (Z = 27): [Ar] $3d^7\ 4s^2$
Co^{2+}: [Ar] $3d^7$ → has three unpaired electrons → paramagnetic
Zn (Z = 30): [Ar] $3d^{10}\ 4s^2$
Zn^{2+}: [Ar] $3d^{10}$ → has 0 unpaired electrons → diamagnetic
Hence, Co^{2+} is attracted to a magnetic field because it has three unpaired electrons.

QUESTION 14.

(i) Give one example each of fibrous protein and globular protein.

(ii) The structures of two amino acids, glycine and alanine, are given below. Draw the peptide linkage between these two amino acids.



(iii) Justify that glucose is an aldose form of sugar, with the help of a chemical reaction.

Ans :

(i) Fibrous protein: Keratin (present in hair, nails, and skin). Other examples include collagen and myosin.
Globular protein: Insulin. Other examples include albumin and haemoglobin.

(ii) $H_2N–CH_2–COOH + H_2N–CH(CH_3)–COOH$
$\downarrow$
$H_2N–CH_2–CO–NH–CH(CH_3)–COOH$
The –CO–NH– bond formed is the peptide linkage.

(iii) Glucose reduces mild oxidising agents like Tollen's reagent, Fehling's reagent indicates the presence of an –CHO (aldehyde) group in glucose. Therefore, glucose is aldose sugar.

QUESTION 15.

Write the chemical reactions when:

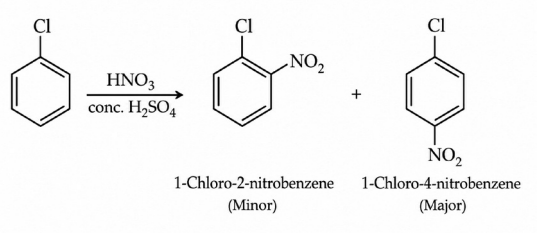
(i) Chlorobenzene is heated with conc. HNO_3 in the presence of conc. H_2SO_4.

(ii) Ethyl alcohol is treated with $SOCl_2$ in the presence of pyridine.

(iii) Chloroform is slowly oxidised with oxygen in the presence of sunlight.

Ans :

(i)



(ii) $C_2H_5OH + SOCl_2 \xrightarrow{\text{(pyridine)}} C_2H_5Cl + SO_2(\uparrow) + HCl(\uparrow)$

(iii) $2CHCl_3 + O_2 \xrightarrow{\text{Sunlight}} 2COCl_2 + 2HCl$

QUESTION 16.

(i) The rate constant of a first order reaction increases five times when the temperature is raised from 350K to 500K. Calculate the activation energy of the reaction. ($R = 8.314\ JK^{-1}mol^{-1}$)

(ii) The unit of rate constant of a reaction is same as that of its rate of reaction. What is the order of this reaction?

Ans :

(i) Given,

$T_1 = 350\ K,\ T_2 = 500\ K,$

$k_2/k_1 = 5;\ R = 8.314\ J\ K^{-1}\ mol^{-1}$

$$\log\left(\frac{k_2}{k_1}\right) = \frac{E_a}{2.303 \times R} \times \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\log 5 = \left(\frac{E_a}{2.303 \times 8.314}\right) \times \left(\frac{1}{350} - \frac{1}{500}\right)$$

$$0.699 = \left(\frac{E_a}{19.147}\right) \times (0.002857 - 0.002000)$$

$$= \left(\frac{E_a}{19.147}\right) \times 0.000857$$

$$= \left(\frac{0.699 \times 19.147}{0.000857}\right)$$

$$= \frac{13.384}{0.000857}$$

$$Ea = 15{,}617\ J\ mol^{-1}$$

$$\approx 15.62\ kJ\ mol^{-1}$$

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(ii) As we know that , The rate constant of a reaction has the same unit as its rate of reaction.
Unit of rate of reaction = mol L^{-1} s^{-1}
As we know that rate law; $R = k[A]^n$
This condition is satisfied only when the reaction is of zero order;

$$n = 0$$

$$[A]^n = [A]^0 = 1$$

Thus, order of reaction is zero.

QUESTION 17.

(i) (a) The molar conductivity at infinite dilution for $\lambda^{\infty}_{H^+} = 348.65$ Scm^2mol^{-1} and for $\lambda^{\infty}_{CH_3COO^-} = 41.4$ Scm^2mol^{-1} respectively.
Calculate the degree of dissociation (α) of acetic acid if its molar conductivity (Λ^c_m) is 40.65 Scm^2mol^{-1}.

(b) Compounds [A] and [B] are two electrolytes. Upon dilution, the molar conductivity of compound [A] increases 3 times while that of [B] increases 30 times. Which one of the two is a weak electrolyte? Why?

(c) Can copper sulphate solution be stored in a zinc pot? Give a reason for your answer by referring to the values given below.

$$E^0_{Zn^{2+}/Zn} = -0.76\ V$$

$$E^0_{Cu^{2+}/Cu} = +0.34\ V$$

Ans :

(a) Given, $\lambda^{\infty}_{H^+} = 348.65$ Scm^2mol^{-1}
$\lambda^{\infty}_{CH_3COO^-} = 41.4$ Scm^2mol^{-1}
$(\Lambda^c_m) = 40.65$ Scm^2mol^{-1}

$$\Lambda^{\circ}_{m(CH_3COOH)} = \lambda^{\circ}_{(H^+)} + \lambda^{\circ}_{(CH_3COO^-)}$$

$$= 348.65 + 41.4$$

$$= 390.05\ S\ cm^2\ mol^{-1}$$

Degree of dissociation is given by

$$\alpha = \frac{\Lambda_m}{\Lambda^{\circ}_m}$$

$$= \frac{40.65}{390.05}$$

$$= 0.1042 \text{ or } 10.42\%$$

(b) Weak electrolytes ionise only partially in solution. On dilution, their degree of ionisation increases significantly, causing a large increase in molar conductivity. While strong electrolytes are already almost completely ionised, so on dilution only a small increase in molar conductivity. Since B shows a much larger increase (30 times), it is the weak electrolyte.

(c) Given, $E^{\circ}_{Zn^{2+}/Zn} = -0.76$ V
$E^{\circ}_{Cu^{2+}/Cu} = +0.34$ V
For the given cell,the cell equation is
$Zn(s) \mid Zn^{2+}(aq) \parallel Cu^{2+}(aq) \mid Cu(s)$

$$E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode}$$

$$= E^{\circ}_{Cu^{2+}/Cu} - E^{\circ}_{Zn^{2+}/Zn}$$

$$= 0.34 - (-0.76)$$

$$= 1.10\ V$$

Since E°_{cell} is positive, the reaction is spontaneous. Therefore, $CuSO_4$ solution cannot be stored in a zinc pot, because zinc pot will react and corrode.

or

(ii) (a) When a current of 0.75 ampere is passed through a $CuSO_4$ solution for 25 minutes, 0.370 g of copper is deposited. Calculate the atomic weight of copper by using the given information.

(b) Two metals A and B have standard reduction potential values, – 0.76 V and + 0.34 V respectively.
Which of these metals will liberate H_2 gas from dil. H_2SO_4? Why?

(c) Why does the specific conductivity (κ) of a solution decrease on dilution?

Ans :

(a) Given,
Current (I) = 0.75 A;
Time (t) = 25 minutes
= 25 × 60 = 1,500 s
Mass of Cu deposited (m) = 0.370 g
Now using Faraday's First Law of Electrolysis:

$$m = ZIt$$

$$= EIt/96{,}500$$

$$0.370 = (E \times 0.75 \times 1{,}500)/96{,}500$$

$$E = (0.370 \times 96{,}500)/1{,}125$$

$$= 31.74$$

Copper is deposited from $CuSO_4$:
$Cu^{2+} + 2e^- \rightarrow Cu$
Valency = 2
Atomic weight = E × 2
= 31.74 × 2
= 63.48 g

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(b) $E^{\circ}_{H^+/H_2} = 0.00$ V

A metal will liberate hydrogen if its standard reduction potential is less than 0 V (i.e., more negative than hydrogen).

$E_A^{\circ} = -0.76$ V → more negative than hydrogen.

$E_B^{\circ} = +0.34$ V → less reactive than hydrogen.

Therefore, Metal A will liberate H_2 gas from dilute H_2SO_4 because it is more easily oxidised than hydrogen.

(c) Specific conductivity is governed by the number of ions present per unit volume. Upon dilution, although the total number of ions may rise (in the case of weak electrolytes), the number of ions contained in a unit volume falls.

As conductivity is determined by the number of ions per unit volume, the specific conductivity therefore decreases on dilution.

QUESTION 18.

Identify the compounds [A], [B] and [C] in the following reactions:

(i) $CH_3CH_2Br \xrightarrow{KCN} [A] \xrightarrow{LiA|H_4} [B] \xrightarrow{HNO_2} [C]$

(ii) $CH_3CH_2COOH \xrightarrow{NH_3} [A] \xrightarrow{\Delta} [B] \xrightarrow{Br_2/KOH} [C]$

Ans :

(i) [A] = CH_3CH_2CN (propanenitrile)
[B] = $CH_3CH_2CH_2NH_2$ (propan-1-amine)
[C] = $CH_3CH_2CH_2OH$ (propan-1-ol) + $N_2\uparrow$ + H_2O

(ii) [A] = $CH_3CH_2COO^-NH_4^+$ (ammonium propanoate)
[B] = $CH_3CH_2CONH_2$ (propanamide)
[C] = $CH_3CH_2NH_2$ (ethylamine)

SECTION D 15 MARKS

QUESTION 19.

(i) Calculate the mass of ascorbic acid (molecular mass = 176 g mol^{-1}) to be dissolved in 75 g of acetic acid to lower its freezing point by 1.5°C. Assume that the solute neither associates nor dissociates in solution.
(K_f for acetic acid = 3.9 K kg mol^{-1})

Ans :

Given,
Molar mass of ascorbic acid = 176 g mol^{-1},
Mass of acetic acid; w_1 = 75 g,

$\Delta T_f = 1.5°C$, $K_f = 3.9$ K kg mol^{-1},

No association or dissociation → $i = 1$
As we know that

$$\Delta T_f = K_f \times \left(\frac{w_2}{M_2}\right) \times \left(\frac{1000}{w_1}\right)$$

$$1.5 = 3.9 \times \left(\frac{w_2}{176}\right) \times \left(\frac{1000}{75}\right)$$

$$= 3.9 \times 1000 \times \frac{w_2}{(176 \times 75)}$$

$$= 3,900 \times \frac{w_2}{13,200}$$

$$w_2 = \frac{(1.5 \times 13,200)}{3,900}$$

$$= \frac{19,800}{3,900} = 5.077 \text{ g}$$

Mass of ascorbic acid = 5.08 g

(ii) A solution of an organic compound was prepared by dissolving 6.8 g in 0.1 litre of water. Calculate the osmotic pressure of this solution at 25°C.
(Molecular mass of organic compound = 321.45 g mol^{-1})

Ans :

Given,

Mass of solute = 6.8 g

Molar mass = 321.45 g mol^{-1}

Volume = 0.1 L

Temperature = 25°C = 298 K

R = 0.0821 L atm mol^{-1} K^{-1}

$$n = \frac{w}{M}$$

$$= \frac{6.8}{321.45} = 0.02116 \text{ mol}$$

$$C = \frac{n}{V}$$

$$= \frac{0.02116}{0.1}$$

$$= 0.2116 \text{ mol L}^{-1}$$

$$\pi = CRT$$

$$\pi = 0.2116 \times 0.0821 \times 298$$

$$= 5.18 \text{ atm}$$

(iii) Why are aquatic species more comfortable in cold water than warm water?

Ans :

According to Henry's Law, gases dissolve more readily in liquids at lower temperatures, since cold water is able to hold more oxygen than warm water. As aquatic organisms rely on dissolved oxygen for their respiration, the greater

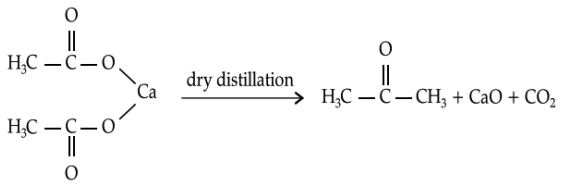
availability of oxygen in cold water makes their survival easier.
When water is warm, the solubility of oxygen falls, which lowers the quantity of dissolved oxygen present. As a result, respiration becomes difficult for aquatic species.
Hence, aquatic species feel more comfortable in cold water than in warm water..

QUESTION 20.

(i) What happens when (write chemical equations):
(a) Calcium acetate is subjected to dry distillation.
(b) Acetaldehyde is reduced with hydrogen in the presence of Zn/Hg and conc. HCl.
(c) Acetic acid is heated with ethyl alcohol in the presence of conc. H_2SO_4.

Ans :

(a)



(b) $CH_3CHO \xrightarrow[\text{conc.HCl}]{\text{Zn}-\text{Hg}} CH_3CH_3(\text{Ethane}) + H_2O$

(c) $C_2H_5OH + CH_3COOH \xrightarrow[H_2SO_4]{\text{Conc.}} CH_3COOC_2H_5 + H_2O$

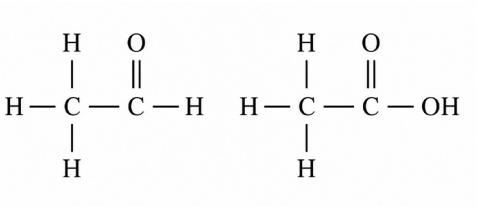
(ii) An organic compound [X] with molecular formula C_2H_4O forms compound [Y] on oxidation. Compound [X] undergoes haloform reaction.
On treatment with HCN, compound [X] forms a product [Z] which on hydrolysis gives 2-hydroxy propanoic acid.
(a) Write down the structures of compounds [X] and [Y].
(b) Name the product formed when [X] reacts with dil. NaOH.

Ans :

(a) The molecular formula of [X] is C_2H_4O. It gives the haloform test, which is shown only by methyl carbonyl compounds, so X must be CH_3CHO (ethanal or acetaldehyde).

$$CH_3CHO + \frac{I_2}{NaOH} \rightarrow CHI_3 \downarrow + HCOONa$$

On oxidation, ethanal converts into the corresponding carboxylic acid CH_3COOH, so compound Y is ethanoic acid.
$CH_3CHO + [O] \rightarrow CH_3COOH$
When X reacts with HCN, it forms a cyanohydrin, $CH_3CH(OH)CN$, which on hydrolysis gives 2-hydroxypropanoic acid; therefore compound Z is $CH_3CH(OH)CN$ (2-hydroxypropanenitrile).
$CH_3CHO + HCN \rightarrow CH_3CH(OH)CN$
$CH_3CH(OH)CN + 2H_2O\ (H^+) \rightarrow CH_3CH(OH)COOH + NH_3$
Structures of compound X and Y are as follows-



(b) This reaction is known as aldol reaction-

$$2CH_3CHO \xrightarrow{\text{dil.NaOH}} CH_3CH(OH)CH_2CHO$$

QUESTION 21.

(i) (a) With reference to Valence Bond Theory (VBT), answer the following questions regarding the complex ion $[Cr(NH_3)_6]^{3+}$.
(1) What is the oxidation number of chromium in the complex?
(2) State the magnetic behaviour of the complex.
(3) How many unpaired electrons are there in the complex?
(4) State the type of hybridisation of the central metal atom.
(b) The coordination complex $CoNO_2Cl_5NH_3$ exists in two isomeric forms 'P' and 'Q'. Isomer 'P' reacts with $AgNO_3$ solution to give white precipitate whereas 'Q' does not give any precipitate with $AgNO_3$ solution.
(1) Write the structural formula of isomers 'P' and 'Q'.
(2) Name the type of isomerism involved.
(c) Explain why an aqueous solution of potassium hexacyanidoferrate(II) does not give the test of ferrous ion.

Ans :

(a) (1) Let the oxidation number of Cr be x. NH_3 is neutral ligand.

$$x + 6(0) = +3$$

$$x = +3$$

Oxidation number of Cr = +3

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(2) Since Cr^{3+} has unpaired electrons, the complex is paramagnetic.

(3) Number of unpaired electrons = 3
Cr^{3+}: $3d^3 \rightarrow t_{2g}\ ^3eg^0$ (in octahedral field with strong ligand NH_3)

(4) NH_3 is a strong field ligand. Two of the inner 3d orbitals combine with one 4s orbital and three 4p orbitals undergo d^2sp^3 hybridisation.
Geometry: Octahedral (inner orbital complex)

(b) (1) P: $[Co(NH_3)_5(NO_2)]Cl$ — NO_2 is in coordination sphere, Cl is free which reacts with $AgNO_3$ to give white precipitate of AgCl.
Q: $[Co(NH_3)_5Cl]NO_2$ — Cl is in coordination sphere, NO_2 is free which does not give precipitate with $AgNO_3$.

(2) Type of isomerism : Ionisation isomerism

(c) An aqueous solution of potassium hexacyanidoferrate (II) $K_4[Fe(CN)_6]$ does not give the test for Fe^{2+} ion because in the complex $[Fe(CN)_6]^{4-}$, the Fe^{2+} ion is bonded to 6 CN^- ligands through strong coordinate bonds. CN^- is a strong field ligand that forms a very stable complex. As a result, there are no free Fe^{2+} ions in solution.

or

(ii) (a) Write the electronic configuration of the following:
(1) d^4 (high spin octahedral)
(2) d^6 (low spin octahedral)

(b) Based on the above configuration, calculate the value of Crystal Field Splitting Energy (CFSE). (Ignore pairing energy)

(c) Name the type of isomerism exhibited by the following pairs of coordination compounds.
(1) $[Co(NH_3)_5(ONO)]Cl_2$ and $[Co(NH_3)_5NO_2]Cl_2$
(2) $[PtCl_2(NH_3)_4]Br_2$ and $[PtBr_2(NH_3)_4]Cl_2$

(d) Which of the following coordination complexes is an outer orbital complex? Explain.
$[Fe(H_2O)_6]^{2+}$ or $[Fe(CN)_6]^{4-}$

Ans :

(a) (1) d^4 high-spin octahedral)
Configuration: $t_{2g}^3eg^1$
Number of unpaired electrons = 4 (paramagnetic)

(2) d^6 low-spin octahedral
configuration: $t_{2g}^6eg^0$
Number of unpaired electrons = 0 (diamagnetic)

(b) For d^4 (high-spin),we can write the following equation,

$$CFSE = (3 \times -0.4\Delta o) + (1 \times 0.6\Delta o)$$
$$= -1.2\Delta o + 0.6\Delta o$$
$$= -0.6\Delta o$$

For d^6 (low-spin), For d^4 (high-spin),we can write the following equation

$$CFSE = 6 \times (-0.4\Delta o)$$
$$= -2.4\Delta o$$

(c) (1) Linkage isomerism
(2) Ionisation isomerism

(d) Oxidation state of Fe in both compounds $[Fe(H_2O)_6]^{2+}$ and $[Fe(CN)_6]^{4-}$ is Fe^{2+}.
$Fe^{2+} \rightarrow d^6$ configuration.
H_2O is a weak field ligand $\rightarrow$ high-spin $\rightarrow$ uses outer orbitals (4d).
CN^- is a strong field ligand $\rightarrow$ low-spin $\rightarrow$ uses inner (3d) orbitals.
Thus, $[Fe(H_2O)_6]^{2+}$ is an outer orbital complex.

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CHAPTER 1

Solution

SUMMARY

1. SOLUTION

A solution is a homogeneous mixture of two or more substances whose composition can be changed within certain fixed limits. Binary solution consists of two components as given below:

1. **Solute :** The component of the solution present in small proportion. It is generally denoted by B.
2. **Solvent :** The component of solution present in large proportion. It is generally denoted by A.

2. CONCENTRATION OF SOLUTION

The concentration of a solution may be expressed in different ways as :

1. **Mass percentage :** Mass of the solute (in g) present in 100 g of a solution.
   For example: 20% H_2SO_4 solution by mass means - Ej

$$w_B = 20\text{ g},\ w_A = 80\text{ g and } w_S = 100\text{ g}$$

(w_S = weight of solution)

$$\text{Mass percentage of } B = \frac{w_B}{w_A + w_B} \times 100$$

2. **Volume percentage :** Volume of the solute (in cc) present in 100 cc of the solution.

$$\text{Volume percentage of } B = \frac{V_B}{V_A + V_B} \times 100$$

3. **Molarity** (M) **:** Number of moles of solute present per litre of the solution.

$$M = \frac{w_B \times 1000}{M_B \times V_S(\text{in cc})}$$

w_B = Mass of solute

M_B = Molecular mass of solute

4. **Molality** (m) **:** Number of moles of solute present in one kg of solvent.

$$m = \frac{w_B \times 1000}{M_B \times w_A(\text{in g})}$$

w_A = Mass of solvent in gram

5. **Normality** (N) **:** Number of gram equivalents of solute present per litre of the solution.

$$N = \frac{w_B \times 1000}{\text{Eq. mass of solute} \times V_S(\text{in cc})}$$

6. **Mole fraction** (x) **:** Ratio of the number of moles of solute or solvent to the total number of moles of the solution.

$$x_A = \frac{n_A}{n_A + n_B}$$

and $$x_B = \frac{n_B}{n_A + n_B};\ x_A + x_B = 1$$

7. **Parts per million** (ppm) **:** Number of the parts by weight of solute in one million parts by weight of the solution.

$$ppm_B = \frac{w_B}{w_S} \times 10^6$$

8 Formality (F) : Number of gram formula masses of solute present in one litre of the solution.

$$F = \frac{w_B \times 1000}{\text{Formula mass of } B \times V_S(\text{in cc})}$$

NOTE :

1. Normality = Molarity × Basicity (For acids)
2. Normality = Molarity × Acidity (For bases)
3. Normality equation : $N_1 V_1 = N_2 V_2$
4. Molarity equation : $M_1 V_1 = M_2 V_2$

   The molarity equation for reaction between two reactants in solution is

$$\frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2}$$

Where n_1 = Number of moles reactant 1,

n_2 = Number of moles of reactant 2

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5. Molarity equation of mixture of solutions:
$$M_1V_1 + M_2V_2 = N_3(V_1 + V_2)$$
6. Normality equation of mixture of solutions:
$$N_1V_1 + N_2V_2 = N_3(V_1 + V_2)$$
7. Equivalent mass of :
$$\text{Acid} = \frac{\text{Molecular Mass}}{\text{Basicity}}$$
$$\text{Base} = \frac{\text{Molecular Mass}}{\text{Acidity}}$$
$$\text{Salt} = \frac{\text{Molecular Mass}}{\text{Total + ve valency of metal ion}}$$
$$\text{Ion} = \frac{\text{Formula Mass of ion}}{\text{Charge}}$$
8. Normality of an acid = Molarity × Basicity
9. Normality of a base = Molarity × Acidity
10. Oxidising and reducing agent
$$= \frac{\text{Molecular mass or at mass}}{\text{Number of } e^- \text{s lost or gained by one molecule of substance}}$$

3. SOLUBILITY OF GASES IN LIQUIDS

Solubility of a gas in liquid is the volume of gas in cc (measured at STP) which dissolves in one litre of the liquid to form a saturated solution at a particular temperature. It depends:

1. **Nature of gas :** Gases like H_2, O_2, N_2 are less soluble in water, while NH_3, CO_2 are more soluble.
2. Nature of the liquid. (like dissolves like)
3. Temperature of the solution.
$$\text{Solubility} \propto \frac{1}{\text{Temperature}}$$
Dissolution of gas in liquid is an exothermic process
4. **Pressure of the gas over solution :** The solubility of a gas in a liquid at a given temperature is directly proportional to the partial pressure of the gas over the solution (Henry's law). Mathematically,
$$m \propto p \text{ or } m = Kp$$
Where K is a constant of proportionality.
Expressing solubility in terms of mole fraction, Henery's Law can be written as
$$x \propto p \text{ or } x = K'p$$
$$p = K_H x$$
Where p is partial pressure of the gas and K_H is called Henry's constant.
$$K_H = \frac{1}{K'}$$
Thus, Henry's law can be defined as - "Partial pressure of a gas in vapour phase (p) is directly proportional to mole fraction (x) of gas in solution".

4. SOLUBILITY OF SOLIDS IN LIQUIDS

Solubility of a solid in a liquid is the maximum amount of the solid (in g) which dissolves in 100 g of the liquid to form a saturated solution at a particular temperature. It depends upon:

1. **Nature of the solute and solvent :** Like dissolves like. Polar solute is soluble in polar solvent and a non-polar, one in a non-polar solvent.
2. **Temperature of the solution :**
For endothermic process,
$$\text{Solubility} \propto \text{Temperature}$$
For exothermic process,
$$\text{Solubility} \propto \frac{1}{\text{Temperature}}$$

5. VAPOUR PRESSURE

The pressure exerted by the vapour of a liquid in equilibrium with the liquid at particular temperature is called its vapour pressure. It depends upon:

(a) **Nature of liquid** : Liquid having strong intermolecular force posses lower vapour pressure at given temperature.
(b) **Temperature :** Vapour pressure increases with increase in temperature
(c) **Presence of impurities :** The presence of non -volatile impurities lowers the vapour pressure while that of volatile impurities raises the vapour pressure of a liquid

6. RAOULT'S LAW

1. **For volatile solute :** In a solution, the V.P. of a component at a given temperature is equal to the mole fraction of that component in the solution multiplied by the V.P. of that component in the pure state.
$$P_A = P^\circ_A x_A,$$
$$P_B = P^\circ_B x_B$$
2. **For non-volatile solutes :** According to this law, "the vapour pressure of a solution containing a non-volatile solute is directly proportional to the mole fraction of solvent".
$$P_S \propto x_A$$

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7. IDEAL SOLUTIONS

The solutions in which the intermolecular interaction between the two components $(A \leftrightarrow B)$ is of the same magnitude as the intermolecular interaction between pure components $A \leftrightarrow A$ and $B \leftrightarrow B$ are called ideal solutions.

Examples : Benzene and Toluene, Hexane and Heptane.

The characteristics of an ideal solution are:

1. It must obey Raoult's law.
2. $\Delta H_{mixing} = 0$.
3. $\Delta V_{mixing} = 0$.

In such solutions, $P_A = P_A^{\circ} x_A$, $P_B = P_B^{\circ} x_B$

8. NON-IDEAL SOLUTIONS

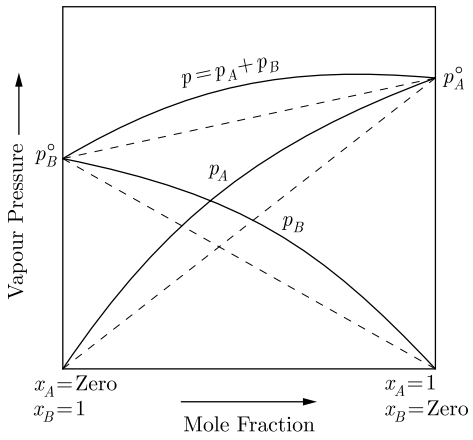
The solutions in which the intermolecular interactions between the two components $(A \leftrightarrow B)$ are of different magnitude as the intermolecular interactions between pure components $A \leftrightarrow A$ and $B \leftrightarrow B$ are called non-ideal solutions.

The characteristics of non-ideal solution are:

1. It does not obey the Raoult's law
2. $\Delta H_{mixing} \neq 0$
3. $\Delta V_{mixing} \neq 0$

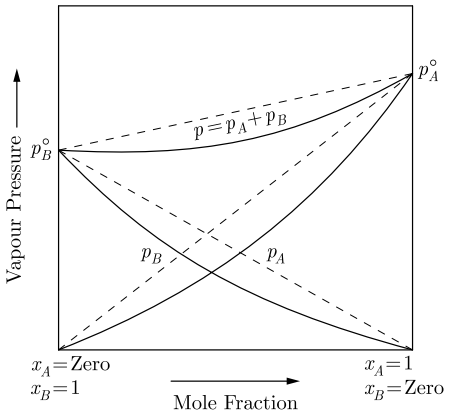
They are of two types:

1. **Non-ideal solution showing positive deviations :** Those solutions in which $(A \leftrightarrow B)$ interactions are weaker than $A \leftrightarrow A$ and $B \leftrightarrow B$ interactions are called non-ideal solutions showing positive deviations.
   Examples : Benzene and acetone, acetone and ethylalcohol. The characteristics of these solutions are:
   (a) $P_A > P^{\circ}{}_A x_A$ and $P^{\circ}{}_B x_B$
   (b) $\Delta H_{mixing} > 0$
   (c) $\Delta V_{mixing} > 0$



Vapour pressure diagram showing positive deviation

2. **Non-ideal solution showing negative deviation :** Those solutions in which $(A \leftrightarrow B)$ interactions are stronger than $A \leftrightarrow A$ and $B \leftrightarrow B$ interactions are called non-ideal solutions showing negative deviations.
   Examples : Acetone and chloroform and aniline. The characteristics of these solutions are
   (a) $P_A < P_A^{\circ} x_A$ and $P_B < P_B^{\circ} x_B$
   (b) $\Delta H_{mixing} < 0$
   (c) $\Delta V_{mixing} < 0$



Vapour pressure diagram showing negative deviation

9. COLLIGATIVE PROPERTIES

Those properties of a solution which depend on the number of solute particles only but not on the nature of the solute are called colligative properties. There are four colligative properties of a solution. These are:

1. **Relative lowering in vapour pressure :** The relative lowering of vapour pressure of a solution is equal to the mole fraction of the solute.

$$\frac{P^{\circ} - P_S}{P^{\circ}} = x_B$$

For very dilute solutions

$$\frac{P^{\circ} - P_S}{P^{\circ}} = \frac{n_B}{n_A}$$

$$\frac{P^{\circ} - P_S}{P^{\circ}} = \frac{\frac{w_B}{M_B}}{\frac{w_A}{M_A}}$$

Also,

$$\frac{P^{\circ} - P_S}{P_S} = \frac{\frac{w_B}{M_B}}{\frac{w_A}{M_A}}$$

(If solution is not dilute)

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2. **Elevation in boiling point :** For a dilute solution, the elevation in boiling point is directly proportional to the molality of the solution.

$$\Delta T_b \propto m$$

$$\Delta T_b = K_b m$$

$$\Delta T_b = K_b \times \frac{w_B}{M_B} \times \frac{1000}{w_A}$$

Where K_b = molal elevation constant.

3. **Depression in freezing point :** For a dilute solution, the depression in freezing point is directly proportional to the molality of the solution.

$$\Delta T_f \propto m$$

$$\Delta T_f = K_f m$$

$$\Delta T_f = K_f \times \frac{w_B}{M_B} \times \frac{1000}{w_A}$$

Where K_f = molal depression constant.

4. **Osmotic pressure :** The pressure which must be applied to the solution side to just prevent the passage of pure solvent into it through a semi permeable membrane

$$\pi = CRT$$

$$\pi = \frac{n_B}{V} RT$$

$$\pi = \frac{w_B RT}{M_B \cdot V}$$

10. ISOTONIC SOLUTIONS

Those solutions which have the same osmotic pressure at the same temperature are called isotonic solutions.

$$\pi_1 = \pi_2$$

11. REVERSE OSMOSIS

If a pressure more than osmotic pressure is applied on the solution side, the solvent will flow from the solution side to solvent side through a semi permeable membrane. This phenomenon is called reverse osmosis.

Example : Desalination of sea water.

12. ABNORMAL MOLECULAR MASSES

Sometimes the observed molecular mass of a substance determined with the help of colligative properties is quite different from the normal molecular mass. This is called abnormal molecular mass.

It is mainly due to the dissociation or association of the solute particles in the solution.

13. VAN'T HOFF FACTOR

NODIA

It is defined as "the ratio of normal molecular mass to the observed molecular mass."

$$i = \frac{\text{Normal molecular mass}}{\text{Obsrved molecular mass}}$$

or $$i = \frac{\text{Observed colligative property}}{\text{Normal colligative property}}$$

If $i = 1$ (Neither association nor dissociation)

For dissociation $i > 1$, For association, $i < 1$

14. DEGREE OF ASSOCIATION

It is defined as the fraction of total number of moles of the substance which associate in solution at equilibrium.

$$\alpha = \frac{m(i-1)}{1-m} \text{ moles,}$$

Where m = number of moles associated.

15. DEGREE OF DISSOCIATION

It is defined as the fraction of total number of moles of the electrolyte which dissociate into ions in solution at equilibrium.

$$\alpha = \frac{i-1}{m-1}$$

Where, m = number of moles dissociated.

16. MODIFIED COLLIGATIVE PROPERTIES

The inclusion of Van't hoff factor modifies the equations for the colligative properties as follows:

1. $\frac{P^\circ - P_S}{P^\circ} = i \cdot x_B$
2. $\Delta T_b = iK_b m$
3. $\Delta T_f = iK_f \cdot m$
4. $\pi = i\,CRT$

OBJECTIVE QUESTIONS

1. Solutions which distil without any change in composition and temperature are called
ISC Specimen 2021-22 (Sem-I)

(a) ideal (b) supersaturated
(c) azeotropic (d) isotonic

Ans : (c) azeotropic
Azeotropic mixture is a constant boiling mixture in which the compositon remains same throughout the boiling.

2. The lowest freezing point of 0.1 M aqueous solution of
ISC 2006

(a) K_2SO_4 (b) NaCl
(c) urea (d) glucose

Ans : (a) K_2SO_4
K_2SO_4 has the lowest freezing point as it dissociates to give more number of particles.

$$K_2SO_4 \rightleftharpoons 2K^+ + SO_4^{2-}$$

3. Colligative properties depend on
ISC Specimen 2021-22 (Sem-I)

(a) the nature of solute particles in solution
(b) the number of solute particles in solution
(c) the nature of solute and solvent particles
(d) the physical properties of solute particles in solution

Ans : (b) the number of solute particles in solution
Colligative properties depend on the total number of solute particles in the solution. It does not depend on the chemical nature of its components.

4. For a dissociated solute in solution, the value of van't Hoff factor is
ISC 2010

(a) zero (b) one
(c) greater than one (d) less than one

Ans : (c) greater than one
For a dissociated solute, one solute particle breaks into two or more ions in solution. As a result, the total number of particles increases. The van't Hoff factor (i) is the ratio of actual particles to expected particles, so for dissociation its value becomes greater than one.

5. An example of intensive property is
ISC 2010

(a) number of moles (b) mass
(c) volume (d) density

Ans : (d) density
An intensive property does not depend on the amount of substance present. Density remains the same whether the sample size is small or large. On the other hand, mass, volume, and number of moles depend on the quantity of matter, so they are extensive properties.

6. According to which law the solubility of a gas at equilibrium and constant temperature varies directly with the pressure of the gas, provided the gas does not undergo any chemical change during the dissolution?
ISC 2021-22 (Sem-I),2008

(a) Raoult's law
(b) Nernst distribution law
(c) Henry's law
(d) van't Hoff law

Ans :
(c) Henry's law

7. A student prepared 1 M HCl solution at 25°C. On heating the solution to 50°C, the molarity will:
ISC 2017

(a) Increase
(b) Decrease
(c) Remain unchanged
(d) Become zero

Ans : (b) Decrease
Volume of solution increases on heating while number of moles remains constant. Since molarity depends on volume of solution, its value decreases with increase in temperature.

8. A scuba diver rises rapidly from deep sea water and experiences breathing difficulty due to formation of gas bubbles in blood. This is explained by:
ISC 2025

(a) Raoult's law
(b) Osmosis
(c) Henry's law
(d) Reverse osmosis

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Ans : (c) Henry's law

At high pressure, more nitrogen dissolves in blood. Sudden decrease in pressure reduces solubility, causing nitrogen bubbles to form. This condition is called decompression sickness or bends.

9. A solution exhibits higher vapour pressure than predicted by Raoult's law. The solution most likely shows:

ISC 2019, 2007

(a) Strong A–B interactions

(b) Association of molecules

(c) Positive deviation

(d) Negative deviation

Ans : (c) Positive deviation

Positive deviation occurs when intermolecular attraction between unlike molecules is weaker. Molecules escape more easily into vapour phase, increasing vapour pressure above the expected value.

10. Ice melts faster when salt is sprinkled over it because:

ISC 2021

(a) Boiling point increases

(b) Freezing point decreases

(c) Vapour pressure increases

(d) Osmotic pressure decreases

Ans : (b) Freezing point decreases

Salt lowers the freezing point of water. Therefore ice melts even below 0°C. This principle is used in snow-covered regions to remove ice from roads.

11. A solution of urea in water has lower vapour pressure than pure water because:

ISC 2002

(a) Urea is volatile

(b) Number of water molecules at surface decreases

(c) Urea increases kinetic energy of water

(d) Intermolecular forces disappear

Ans : (b) Number of water molecules at surface decreases

Non-volatile urea occupies surface positions and reduces escaping tendency of water molecules. Hence vapour pressure of solution becomes lower than that of pure water.

12. Which solution will show maximum osmotic pressure at the same concentration?

ISC 2025

(a) Glucose solution

(b) Urea solution

(c) NaCl solution

(d) Sucrose solution

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Ans : (c) NaCl solution

NaCl dissociates into Na^+ and Cl^- ions, producing more particles. Osmotic pressure depends on total number of particles present in solution.

13. A solution containing acetone and chloroform shows negative deviation from Raoult's law because:

ISC 2023, 2009

(a) A–B interactions are weak

(b) Molecules dissociate completely

(c) Strong hydrogen bonding develops

(d) Vapour pressure becomes zero

Ans : (c) Strong hydrogen bonding develops

Strong intermolecular attraction between acetone and chloroform molecules decreases escaping tendency, lowering vapour pressure below Raoult's law prediction.

14. A student adds sugar to water and notices that boiling point increases. The increase occurs because:

ISC 2010

(a) Vapour pressure of solution decreases

(b) Sugar evaporates rapidly

(c) Surface tension becomes zero

(d) Density decreases

Ans : (a) Vapour pressure of solution decreases

Addition of non-volatile solute lowers vapour pressure. Therefore higher temperature is needed for vapour pressure to equal atmospheric pressure, increasing boiling point.

15. Which observation confirms that a solution is non-ideal?

ISC 2022, 2016

(a) $\Delta H_{mix} = 0$

(b) Vapour pressure obeys Raoult's law

(c) Volume changes during mixing

(d) Intermolecular forces remain same

Ans : (c) Volume changes during mixing

Non-ideal solutions show either expansion or contraction in volume during mixing because intermolecular interactions between components differ significantly.

16. A concentrated sugar solution is separated from pure water using a semipermeable membrane. Water moves towards sugar solution due to:

ISC 2021, 2017

(a) Reverse osmosis

(b) Diffusion

(c) Osmosis

(d) Sublimation

Ans : (c) Osmosis

Solvent molecules naturally move from lower solute concentration to higher solute concentration through a semipermeable membrane. This process is called osmosis.

17. Which solution will show least depression in freezing point for equal molal concentrations?

ISC 2024

(a) $Al_2(SO_4)_3$

(b) KCl

(c) Glucose

(d) NaCl

Ans : (c) Glucose

Glucose does not dissociate into ions, producing minimum particles. Since depression in freezing point depends on number of particles, glucose shows least depression.

18. Carbonated beverages are sealed under high pressure because:

ISC 2013

(a) Solubility of gas decreases with pressure

(b) Solubility of CO_2 increases with pressure

(c) Boiling point of liquid decreases

(d) Density becomes constant

Ans : (b) Solubility of CO_2 increases with pressure

According to Henry's law, solubility of a gas increases with increase in pressure. Hence soft drinks are bottled under high CO_2 pressure.

19. A solution has Van't Hoff factor less than 1. This indicates:

ISC 2024

(a) Dissociation of solute

(b) Association of solute particles

(c) Ideal behaviour

(d) Complete ionisation

Ans : (b) Association of solute particles

Association decreases total number of particles in solution. Therefore observed colligative properties become smaller, making Van't Hoff factor less than 1.

20. An antifreeze solution is added to car radiators during winter because it:

ISC 2012, 2004

(a) Raises freezing point of water

(b) Lowers boiling point of water

(c) Lowers freezing point of water

(d) Increases vapour pressure

Ans : (c) Lowers freezing point of water

Antifreeze substances decrease freezing point of radiator water, preventing solidification during extremely cold weather conditions.

21. Which of the following pairs is expected to behave nearly ideally?

ISC 2017

(a) Water and ethanol

(b) Benzene and toluene

(c) Acetone and chloroform

(d) HCl and water

Ans : (b) Benzene and toluene

Benzene and toluene have similar molecular size and intermolecular forces. Therefore intermolecular attractions remain nearly unchanged after mixing.

22. A student observes that vapour pressure of a liquid decreases after adding a non-volatile solute. This happens because:

ISC 2020, 2004

(a) Solute molecules escape faster

(b) Solvent molecules at surface decrease

(c) Solvent becomes volatile

(d) Atmospheric pressure changes

Ans : (b) Solvent molecules at surface decrease

Non-volatile solute particles occupy surface positions and reduce number of solvent molecules escaping into vapour phase, thereby lowering vapour pressure.

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23. Which colligative property is most suitable for determining molar mass of proteins?
ISC 2014

(a) Relative lowering of vapour pressure
(b) Elevation in boiling point
(c) Osmotic pressure
(d) Depression in freezing point

Ans : (c) Osmotic pressure
Osmotic pressure measurements are carried out at room temperature and give accurate values even for large biomolecules like proteins.

24. A solution containing dissolved salt boils at a higher temperature than pure water because:
ISC 2016

(a) Salt increases atmospheric pressure
(b) Vapour pressure of solution decreases
(c) Density becomes very high
(d) Water molecules decompose

Ans : (b) Vapour pressure of solution decreases
Lower vapour pressure means more heating is required for vapour pressure to equal atmospheric pressure, causing boiling point elevation.

25. Reverse osmosis differs from osmosis because in reverse osmosis:
ISC 2023

(a) Solvent moves naturally
(b) Solute crosses membrane
(c) External pressure greater than osmotic pressure is applied
(d) Membrane becomes permeable to solute

Ans : (c) External pressure greater than osmotic pressure is applied
In reverse osmosis, pressure exceeding osmotic pressure forces solvent to move opposite to natural osmotic direction. This principle is used in water purification.

26. If molality of the dilute solution of a non-volatile, non-dissociating and non-associating electrolyte is doubled, the value of molal elevation constant or Ebullioscopic constant (K_b) will be
ISC Specimen 2021-22 (Sem-I)

(a) doubled (b) halved
(c) tripled (d) unchanged

Ans : (d) unchanged
The ebullioscopic constant (K_b) is a property of the solvent only and does not depend on the molality or concentration of the solution. Even if the molality of the solution is doubled, the value of K_b remains the same because it depends only on the nature of the solvent.

27. Complete the following statement by selecting the correct alternative from the given choices of the following terms used for denoting concentration of a solution, the one which does not get affected by temperature is
ISC 2014

(a) molarity (b) molality
(c) normality (d) formality

Ans : (b) molality
Molality does not get affected by temperature because molality does not depend on the volume while other three terms depend on the volume and volume varies with temperature.

28. Two aqueous solutions P and Q contain equal masses of glucose and NaCl respectively in equal volumes. Which statement is correct regarding their boiling points?
ISC 2004

(a) P has higher boiling point
(b) Q has higher boiling point
(c) Both have same boiling point
(d) Boiling point cannot be predicted

Ans : (b) Q has higher boiling point
NaCl dissociates into ions, increasing the number of solute particles. Since elevation in boiling point depends on particle number, NaCl solution shows greater boiling point elevation than glucose solution.

29. The molal freezing point constant of water is $1.86\ \text{K kg mol}^{-1}$. Therefore, the freezing point of 0.1 m NaCl solution in water is expected to be
ISC Specimen 2018

(a) -1.86°C (b) -0.372°C
(c) -0.186°C (d) $+0.372^\circ\text{C}$

Ans : (c) -0.186°C
Given, $K_f = 1.86\ \text{K kg mol}^{-1}$
Molality of NaCl = 0.1 m
Depression in freezing point,

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$$\Delta T_f = K_f \times m = 1.86 \times 0.1$$
$$\Delta T_f = 0.186$$
$$\Delta T_f = 0 - T_f = 0 - 0.186$$

30. The molal freezing point constant of water is 1.86 K kg mol^{-1}. Therefore, the freezing point of 0.1 M NaCl solution in water is expected to be

(a) -1.86°C (b) -0.372°C

(c) -0.186°C (d) $+0.372^\circ$C

ISC 2015

Ans : (c) -0.186°C

The molal freezing point constant of water is 1.86 K kg mol^{-1}.

Assume that molality = molarity

Then $m = 0.1$ M

From equation, $\Delta T_f = K_f \times$ molality

$= 1.86$ K kg mol$^{-1} \times 0.1$

$= 0.186$ K $= 0.186^\circ$ C

Depression in freezing point is -0.186° C.

31. The value of molal depression constant or cryoscopic constant (K_f) depends on which of the following ?

ISC 2021-22 (Sem-I)

(a) Nature of solvent

(b) Heat of the solution of the solute in the solvent

(c) Nature of solute

(d) Vapour pressure of the solution

Ans : (a) Nature of solvent

The molal depression constant or cryoscopic constant (K_f) is a property of the solvent only. It does not depend on the nature of the solute or concentration of the solution. Different solvents have different values of K_f because the constant depends on properties like latent heat of fusion and melting point of the solvent.

32. A solution containing components A and B follows Raoult's law.With reference to the statement which of the following options is correct?

ISC 2021-22 (Sem-I)

(a) A—B attraction force is greater than A—A and B—B.

(b) A—B attraction force is less than A—A and B—B.

(c) A—B attraction force remains the same as A—A and B—B.

(d) Total volume of solution is different from sum of volumes of both components A and B.

Ans : (c) A—B attraction force remains the same as A—A and B—B.

The solution which obey Raoult's law is always ideal solution. In ideal solution, attraction force remains same in A—A and B—B.

33. A solution of urea (molecular mass = 60) contains 8.6 g per litre. It is isotonic with a 5% solution of a non-volatile and non-electrolytic solute. What will be the molecular mass of the solute?

ISC 2021-22 (Sem-1)

(a) 34.9 g mol^{-1} (b) 349 g mol^{-1}

(c) 861 g mol^{-1} (d) 3490 g mol^{-1}

Ans : (b) 349 g mol^{-1}

No. of moles of urea $= \frac{8.6}{60}$

5% of unknown solution

$$= \frac{5}{100 \text{ mL}} = \frac{50}{1000 \text{ L}}$$
$$= 5 \text{ g/L}$$

No. of moles of unknown solute $= \frac{50}{m}$

$$\frac{8.6}{60} = \frac{50}{m}$$
$$m = 348.9 \sim 349 \text{ g/mol}$$

34. The molecular weight of sodium chloride determined by measuring the osmotic pressure of its aqueous solution is

ISC 2009

(a) double the theoretical value

(b) same as the theoretical value

(c) half the theoretical value

(d) three times the theoretical value

Ans : (c) half the theoretical value

Molecular weight of NaCl determined by measuring the osmotic pressure of its aqueous solution is half the theoretical value, because it is a strong electrolyte and dissociates into 2 ions.

$$\text{NaCl} \longrightarrow \text{Na}^+ + \text{Cl}^-$$

According to van't Hoff factor, observed molecular mass

$$= \frac{\text{Normal molecular mass}}{\text{Number of particles per molecule}}$$
$$= \frac{\text{Normal molecular mass}}{2}$$

NODIA

35. Out of the following solutions, the one having the highest boiling point will be

ISC 2011

(a) 0.1 M NaCl

(b) 0.1 M $BaCl_2$

(c) 0.1 M KNO_3

(d) 0.1 M $K_4[Fe(CN)_6]$

Ans : (d) 0.1 M $K_4[Fe(CN)_6]$

0.1 M $K_4[Fe(CN)_6]$ has highest boiling point. It is because, $K_4[Fe(CN)_6]$ dissociates to give maximum number of particles as follows

$$K_4[Fe(CN)_6] \longrightarrow 4K^+ + [Fe(CN)_6]^{4-}$$

Therefore, its solution has highest boiling point. Hence, option (d) is correct.

36. A binary solution contains 92 g ethyl alcohol and 72 g water (Atomic weight of C =12, H = 1, O = 16).

ISC Specimen 2021-22, (Sem-I)

(i) Mole fraction of ethyl alcohol is

(a) 0.40 (b) 0.80

(c) 0.66 (d) 0.33

Ans : (d) 0.33

$$\text{No. of moles} = \frac{\text{Given mass}}{\text{Molar mass}}$$

$$\text{Moles of ethyl alcohol} = \frac{92}{46} = 2 \text{ mol}$$

$$\text{Moles of water} = \frac{72}{18} = 4 \text{ mol}$$

$$\text{Mole fraction of ethyl alcohol} = \frac{2}{2+4} = \frac{1}{3} \simeq 0.33$$

(ii) Mole fraction of water is

(a) 0.33 (b) 0.66

(c) 0.20 (d) 0.80

Ans : (b) 0.66

$$\text{Mole fraction of water} = \frac{4}{2+4} = 0.66$$

37. If 5.85 g of NaCl are dissolved in 90 g of water, the mole fraction of solute is

ISC Specimen 2021-22 (Sem-1)

(a) 0.2632 (b) 0.0102

(c) 0.0196 (d) 0.1045

Ans : (c) 0.0196

$$w = 5.85 \text{ g}$$

$$\text{Weight of water} = 90 \text{ g}$$

Mole fraction of NaCl

$$= \frac{\text{No. of moles of NaCl}}{\text{Moles of water + moles of NaCl}}$$

$$= \frac{\frac{\text{Mass of NaCl}}{\text{Molar mass of NaCl}}}{\frac{\text{Mass of water}}{\text{Molar mass of water}} + \frac{\text{Mass of NaCl}}{\text{Molar mass of NaCl}}}$$

$$= \frac{\frac{5.85}{585}}{\frac{90}{18} + \frac{5.85}{58.8}} = 0.0196$$

38. An aqueous solution containing one gram of urea (molecular weight = 60) boils at 100.25°C. The same solution freezes at −0.894°C.The aqueous solution containing 3 g of glucose (molecular weight = 180) in the same volume of solution

ISC Specimen 2021-22 (Sem-I)

(i) What is the boiling point of glucose?

(a) 100.75°C (b) 100.50°C

(c) 100.25°C (d) 100.08°C

(ii) What is the freezing point of glucose?

(a) +0.894° C (b) −0.894° C

(c) +0.447° C (d) −0.447° C

Ans :

$$\text{Moles of urea} = \frac{1}{60} \text{ mol}$$

$$\text{Moles of glucose} = \frac{3}{180} = \frac{1}{60} \text{ mol}$$

When moles are same, then molality is also similar and K_b and K_f will remain unchanged.

Thus, temperature will also remain unchanged.

(i) (c) Boiling point of glucose is 100.25° C.

(ii) (b) And freezing point of glucose is −0.894° C

39. 5 moles of sucrose (molecular mass = 342 g mol^{-1}) dissolved in 1000 g of water (molecular mass = 18 g mol^{-1}). Vapour pressure of pure water at 298 K = 4.57 mm Hg.

ISC 2021-22 (Sem-I)

(i) What will be the vapour pressure of sucrose solution at the same temperature?

(a) 0.419 mm Hg (b) 6.570 mm Hg

(c) 4.190 mm Hg (d) 0.657 mm Hg

Ans : (c) 4.190 mm Hg

According to Raoult's law,

$$p_{\text{solution}} = p^{\circ}_{\text{solvent}} \times \chi_{\text{solvent}}$$

$$= 4.57 \times \frac{\frac{1000}{18}}{\frac{1000}{18} + 5}$$

$$= 4.57 \times \frac{55.55}{55.55 + 5}$$

$$= 4.192 \text{ mm of Hg}$$

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(ii) What will be the mole fraction of sucrose in water?

(a) 0.8261 (b) 0.0826

(c) 0.4376 (d) 0.0435

Ans : (b) 0.0826

Mole fraction of sucrose

$$= \frac{\text{No. of moles of sucrose}}{\text{Moles of sucrose} + \text{Moles of water}}$$

$$= \frac{5}{5 + \frac{1000}{18}} = 0.0826$$

40. A solution contains 54 g of glucose (molecular mass $= 180\,\text{g mol}^{-1}$) in 250 g of water (K_f for water $= 1.86\,\text{K kg mol}^{-1}$).

ISC 2021-22 (Sem-I)

(i) What will be the freezing point of this glucose solution?

(a) 276.402 K (b) 270.768 K

(c) 370.402 K (d) 272.563 K

Ans : (b) 270.768 K

Given, $K_f = 1.86\,\text{K kg mol}^{-1}$; $m = 1.2\,\text{mol kg}^{-1}$

$$\Delta T_f = K_f \times m$$

$$= 1.86\,\text{K kg mol}^{-1} \times 1.20\,\text{mol kg}^{-1}$$

$$= 2.232\,\text{K}$$

$$T_f = T_f' - \Delta T_f = 273\,\text{K} - 2.232\,\text{K}$$

$$= 270.768\,\text{K}$$

(ii) What will be the molality of this glucose solution?

(a) 1.20 m (b) 0.12 m

(c) 2.40 m (d) 0.24 m

Ans : (a) 1.20 m

Weight of glucose$(w) = 54\,\text{g}$

Molecular mass of glucose

$$(M') = 180\,\text{g/mol}$$

Mass of water $(W) = 250\,\text{g}$

$$\text{Molality } (m) = \frac{w \times 1000}{M' \times W(g)}$$

$$= \frac{54 \times 1000}{180 \times 250} = 1.20\,\text{m}$$

41. 0.76 g of glucose (molecular mass $= 180\,\text{g mol}^{-1}$) is dissolved in 20 mL of aqueous solution at 298 K.

($R = 0.0821\,\text{L} - \text{atm K}^{-1}\,\text{mol}^{-1}$)

ISC 2021-22 (Sem-I)

(i) What is the osmotic pressure of solution at 298 K?

(a) 8.41 atm (b) 0.48 atm

(c) 4.89 atm (d) 5.16 atm

(ii) What is the molarity of the glucose solution?

(a) 0.42 M (b) 0.21 M

(c) 4.01 M (d) 2.02 M

Ans :

$\pi = CRT$

where, π = osmotic pressure

R = gas constant $= 0.082\,\text{dm}^3\text{atm mol}^{-1}\text{K}^{-1}$

T = temperature $= 298\,\text{K}$

C = molarity $= \frac{n}{V} = \frac{w}{M \times V}$

where, n = no. of moles

w = weight of solute glucose $= 0.76$ g

M = molecular weight of solute glucose

$= 180$ g

V = volume of solution

$= 2011\,\text{mL} = 0.02\,\text{L}$

(i) (c) $\pi = 0.2 \times 0.0821 \times 298 = 4.89\,\text{atm}$

i.e. option (c) is correct.

(ii) (b) $C = \frac{0.76}{180 \times 0.02} = 0.211\,\text{M}$

i.e. option (b) is correct.

42. A solution of sucrose (molecular weight $342\,\text{g mol}^{-1}$)has been prepared by dissolving 68.4 g of sucrose in 1000 g of water.

(K_f for water $= 1.86\,\text{K kg mol}^{-1}$)

ISC Specimen 2021-22 (Sem-I)

(i) The freezing point of the solution obtained will be

(a) – 0.52° C (b) + 0.52° C

(c) – 0.372° C (d) + 0.372° C

Ans : (c) – 0.372°C

Molecular weight $= 342\,\text{g mol}^{-1}$

Amount of sucrose $= 68.4\,\text{g}$

Amount of water $= 1000\,\text{g}$

K_f for water $= 1.86\,\text{K kg mol}^{-1}$

$$\Delta T_f = K_f \times m \text{ also} \left(\text{also } m = \frac{w_B \times 1000}{M_B \cdot W_A}\right)$$

$$= \frac{1.86 \times 68.4 \times 1000}{342 \times 1000}$$

$$\Delta T_f = 1.86 \times 0.2 = 0.372\,\text{K}$$
$$T_f' - T_f = 0.372$$
$$273 - T_f = 0.372\,\text{K}$$
$$T_f = 273 - 0.372 = 272.628\,\text{K}$$
$$T_b = 273 - 272.628$$
$$= -0.372^\circ\,\text{C}$$

(ii) The molality of sucrose solution will be

(a) 0.1 (b) 0.2

(c) 0.3 (d) 0.4

Ans : (b) 0.2

$$\text{Molality } (m) = \frac{w \times 1000}{M' \times W(g)}$$
$$= \frac{68.4 \times 1000}{342 \times 1000} = 0.2\,\text{m}$$

43. An aqueous solution of urea freezes at $-0.186^\circ\,\text{C}$,K_f for water $= 1.86\,\text{K kg mol}^{-1}$, K_b for water $= 0.522\,\text{K kg mol}^{-1}$. The boiling point of urea solution will be

ISC 2018

(a) 375.065 K (b) 373.186 K

(c) 375.512 K (d) 373.0512 K

Ans : (d) 373.0512 K

Freezing point of the solution,

$$T_f = -0.186^\circ\,\text{C}$$

Converting in Kelvin,

$$T_f = -0.186 + 273$$
$$= 272.814\,\text{K}$$

As $T_f = T_f^o - \Delta T_f$

$$272.814 = 273 - \Delta T_f$$
$$\Delta T_f = 0.186\,\text{K}$$

Now, calculate molality of solution by using the formula

$$\Delta T_f = K_f m$$
$$0.186\,\text{K} = 1.86\,\text{K kg mol}^{-1} \times m$$
$$m = 0.1\,\text{mol kg}^{-1}$$

To calculate elevation in boiling point, we use

$$\Delta T_b = K_b m$$

Given, $K_b = 0.512\,\text{K kg mol}^{-1}$

$$m = 0.1\,\text{mol kg}^{-1}$$
$$\Delta T_b = 0.512\,\text{K kg mol}^{-1} \times 0.1\,\text{mol kg}^{-1}$$
$$\Delta T_b = 0.0512\,\text{K}$$

Boiling point of a solution

$$(T_b) = T_b^o + \Delta T_b$$
$$= (373 + 0.0512)\,\text{K}$$
$$= 373.0512\,\text{K}$$

FILL IN THE BLANK

44. The _____ of the boiling point of solvent by the addition of a solute is _____ proportional to the molality of the solutions.

ISC 2009

Ans :

The elevation of the boiling point of a solvent by the addition of a solute is directly proportional of the molarity of the solution.

i.e. $\Delta T_b \propto m$

45. Solutions which strictly obey _____ law are called _____solutions.

ISC 2012

Ans :

Solutions which strictly obey Raoult's law are called ideal solutions.

46. The _____ pressure of an aqueous solution of 0.1 M cane sugar is _____ than that of pure water.

ISC 2010

Ans :

The vapour pressure of an aqueous solution of 0.1 M cane sugar is less than that of pure water (as it is non-volatile solute.

ONE MARK QUESTIONS

DIRECTION : Correct the following statement.

47. "Molarity of a solution is independent of temperature".

ISC 2005

Ans :

The correct statement is

"Molarity of a solution depends on temperature".

48. "Osmotic pressure and boiling point are colligative properties."

ISC 2004

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Ans :

Osmotic pressure and elevation in boiling point are colligative properties.

49. "Addition of sodium chloride lowers the boiling point and freezing point of water."

ISC 2025

Ans :

Addition of sodium chloride increases the boiling point and decreases the freezing point of water.

50. "Freezing point of a solution is directly proportional to its molality."

ISC 2001

Ans :

Depression in freezing point of a solvent is directly proportional to its molality.

i.e. $\Delta T_f \propto m$

51. Water boils below 100°C by the addition of NaCl.

ISC 2008

Ans :

The correct statement is as follows :

Water boils above 100° C by the addition of NaCl. It is because, NaCl is a strong electrolyte and it dissociates into 2 ions, therefore its van't Hoff value, i is 2 and the elevation of boiling point ΔT_b, is proportional to i.

TWO MARKS QUESTIONS

52. During winter, salt is spread over icy roads in cold countries. Explain the reason behind this practice.

ISC 2004

Ans :

Salt lowers the freezing point of water. Therefore ice melts even below 0°C, preventing accumulation of snow and reducing chances of accidents on roads.

53. A student observes that molarity of a solution changes on heating, while molality remains constant. Explain.

ISC 2021, 2016

Ans :

Molarity depends on volume of solution, which changes with temperature due to expansion. Molality depends on mass of solvent, which remains unaffected by temperature change.

54. Why is osmotic pressure preferred for determining molar masses of proteins and biomolecules?

ISC 2010

Ans :

Proteins have very high molar masses and are sensitive to heat. Osmotic pressure measurements are carried out at room temperature and give accurate results even for dilute solutions.

55. A solution has Van't Hoff factor less than 1. What does this indicate about the solute particles?

ISC 2006

Ans :

It indicates association of solute particles in solution. Smaller particles combine to form larger aggregates, reducing total number of particles present in the solution.

56. A student dissolves sugar in water and notices that vapour pressure decreases. Explain this observation.

ISC 2024

Ans :

Sugar is a non-volatile solute and reduces the number of water molecules escaping from the surface into vapour phase, thereby lowering vapour pressure of the solution.

57. Why do benzene and toluene form nearly ideal solutions whereas acetone and ethanol do not?

ISC 2008

Ans :

Benzene and toluene possess similar molecular sizes and intermolecular forces. Acetone and ethanol have different intermolecular attractions, causing deviation from ideal solution behaviour.

58. A student stores a bottle of soft drink in the sun. After opening, the drink produces excessive bubbles. Explain the reason.

ISC 2025

Ans :

Increase in temperature decreases the solubility of CO_2 gas in the liquid. When the bottle is opened, pressure decreases suddenly and dissolved gas escapes rapidly in the form of bubbles.

59. Two solutions of glucose and NaCl have same molality. Which solution will show greater boiling point and why?

ISC 2025

NODIA

Ans :

NaCl solution will show greater boiling point because NaCl dissociates into ions, increasing the number of solute particles. Greater particle concentration causes larger elevation in boiling point.

60. A mixture of acetone and chloroform shows lower vapour pressure than expected. What conclusion can be drawn about intermolecular interactions?

ISC 2018

Ans :

The solution shows strong intermolecular attraction between unlike molecules. Hydrogen bonding develops between acetone and chloroform molecules, causing negative deviation from Raoult's law.

61. Sea water is not suitable for direct consumption, but reverse osmosis plants make it drinkable. Explain the principle involved.

ISC 2015, 2008

Ans :

In reverse osmosis, pressure greater than osmotic pressure is applied on sea water. Pure water passes through semipermeable membrane while dissolved salts and impurities remain behind.

62. What is a colligative property? Give two examples.

ISC 2003

Ans :

The properties of dilute solutions which depend only on the number of solute particles but not upon their nature are called colligative properties.

Two colligative properties of solutions are

(i) Relative lowering of vapour pressure

(ii) Elevation in boiling point.

63. The osmotic pressure of 0.25 M urea solution is 2.67 atm. What will be the osmotic pressure of a 0.25 M solution of potassium sulphate?

ISC 2010

Ans :

Osmotic pressure, $\pi = iCRT$ where, i is van't Hoff factor.

Value of i for urea is 1 (one) while i for potassium sulphate is 3(strong electrolyte). Also, molarity, M for the two solutions is same (0.25 M).

$$\pi_{(K_2SO_4\,soution)} = i \times \pi_{urea} = 3 \times 2.67 = 8.01\,atm$$

$$(as\ \pi_{urea} = 2.67\ atm)$$

64. Why does soda water fizz when the bottle is opened? Name the law that explains this phenomenon.

ISC 2004

Ans :

Soda water is prepared by dissolving CO_2 in water under a pressure of 5 to 10 atm. The bottle is tightly capped to prevent the escape of CO_2. When the bottle is opened, the pressure reduced and most of the dissolved CO_2 gas escapes from the solution in the form of fizz or effervescence. This phenomenon is based upon Henry's law of solubility of gases. This law states that, 'at constant temperature, the solubility of gas in a liquid is directly proportional to the pressure of the gas.'

65. 0.1 M urea solution shows less depression in freezing point than 0.1 M $MgCl_2$ solution. Explain.

ISC 2024

Ans :

Depression in freezing point is a colligative property which depends on the number of particles. Urea is a molecular compound, it remains as a single molecule. In solution magnesium chloride is an ionic compound, it ionises as follows to give three particles.

$$MgCl_2 \longrightarrow Mg^{2+} + 2Cl^-$$

Thus, 0.1M urea solution shows less depression in freezing point than 0.1 M $MgCl_2$ solution.

66. The elevation in boiling point produced by dilute equimolar solution of three substances are in the order $A >$ glucose $> B$. Suggest a reason for this observation.

ISC 2010

Ans :

Elevation in boiling point is a colligative property which depends upon number of particles of non-volatile solute present in the solution. Larger the molecular mass of the solute, smaller is the value of elevation in boiling point.

On dissociation, molecular mass of the solute decreases while elevation in boiling point rises and vice-versa. Thus, the reason for the given observation in substance A dissociates while substance B associates in the solution.

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67. The molecular weights of sodium chloride and glucose are determined by the depression of freezing point method. Compared to their theoretical molecular weight, what will be their observed molecular weights when determined by the above method? Justify your answer.

ISC 2007

Ans :

Observed molecular mass of sodium chloride will be half of its theoretical mass.

This is because depression in freezing point method is a colligative property which depends upon the number of solute particles present in solution.

One molecule of sodium chloride furnishes two particle, Na^+ and Cl^- in aqueous solution as it is a strong electrolyte.

$$NaCl \longrightarrow Na^+ + Cl^{-1}$$

According to van't Hoff factor, observed molecular mass

$$= \frac{\text{Normal molecular mass}}{\text{Number of particles formed per molecule}}$$

Observed molecular mass of glucose as determined by the depression of freezing point method will be same as its theoretical molecular mass. It is because glucose neither shows association nor dissociation in aqueous solution as it is a weak electrolyte.

THREE MARKS QUESTIONS

68. A bottle of cold drink fizzes vigorously when opened on a hot day. Explain the phenomenon using Henry's law.

ISC 2023

Ans :

According to Henry's law, solubility of a gas in a liquid is directly proportional to the pressure of the gas above the liquid. Cold drinks are bottled under high pressure so that large amount of CO_2 dissolves in the liquid. On a hot day, increase in temperature decreases the solubility of CO_2. When the bottle is opened, pressure suddenly decreases and dissolved gas escapes rapidly in the form of bubbles and fizz.

69. Explain why vapour pressure of a solution containing non-volatile solute is lower than that of pure solvent.

ISC 2025

Ans :

A non-volatile solute does not itself enter the vapour phase. When such a solute is added to a solvent, some surface positions become occupied by solute particles. As a result, the number of solvent molecules escaping from the surface decreases. Consequently, vapour pressure of the solution becomes lower than that of the pure solvent. This phenomenon is explained by Raoult's law.

70. Acetone and chloroform show negative deviation from Raoult's law. Explain.

ISC 2017

Ans :

Acetone and chloroform form strong hydrogen bonds between unlike molecules. These intermolecular attractions are stronger than those present in the pure liquids. Due to stronger attraction, molecules escape less easily into vapour phase. Therefore the vapour pressure of the solution becomes lower than the value predicted by Raoult's law. Hence the solution shows negative deviation from ideal behaviour.

71. Why does NaCl solution show greater elevation in boiling point than glucose solution of same concentration?

ISC 2010

Ans :

NaCl is an electrolyte and dissociates into Na^+ and Cl^- ions in aqueous solution. Thus, one formula unit of NaCl produces two particles. Glucose is a non-electrolyte and does not dissociate in water. Since elevation in boiling point depends upon the number of solute particles present, NaCl solution produces greater boiling point elevation than glucose solution of the same concentration.

72. Explain why molality is preferred over molarity in colligative property calculations.

ISC 2024

Ans :

Molality is defined in terms of mass of solvent, whereas molarity is defined in terms of volume of solution. Volume changes with temperature due to expansion or contraction, but mass remains constant. Since colligative properties are temperature dependent, concentration should also remain unaffected by temperature changes. Therefore molality is preferred over molarity for accurate calculations involving colligative properties.

NODIA

73. Explain the principle of reverse osmosis used in water purification.

ISC 2019

Ans :

In normal osmosis, solvent flows from pure solvent side to solution side through a semipermeable membrane. In reverse osmosis, pressure greater than osmotic pressure is applied on the solution side. This forces solvent molecules to move in the reverse direction through the membrane. Dissolved salts and impurities remain behind, while pure water is obtained. This principle is widely used in desalination and domestic water purifiers.

74. Why do benzene and toluene form nearly ideal solutions?

ISC 2011

Ans :

Benzene and toluene possess similar molecular sizes, structures and intermolecular forces. Therefore, intermolecular attractions between unlike molecules are nearly equal to those between like molecules. As a result, mixing does not involve appreciable heat or volume change. Such solutions obey Raoult's law throughout the concentration range and are therefore considered nearly ideal solutions.

75. Explain why solubility of gases in liquids decreases with increase in temperature.

ISC 2024

Ans :

Dissolution of gases in liquids is generally an exothermic process because heat is released when gas molecules dissolve. According to Le Chatelier's principle, increase in temperature favours the reverse process, namely escape of gas molecules from the solution. Therefore solubility of gases decreases with increase in temperature. This is why aquatic organisms face difficulty in respiration during summer season.

76. A solution shows positive deviation from Raoult's law. What does this indicate about intermolecular interactions?

ISC 2021

Ans :

Positive deviation from Raoult's law indicates that intermolecular attractions between unlike molecules are weaker than those between like molecules. Due to weaker attraction, molecules escape more easily into vapour phase. Consequently, vapour pressure becomes greater than the value predicted by Raoult's law. Such solutions generally show increase in volume and absorption of heat during mixing.

NODIA

77. Explain why osmotic pressure is considered a colligative property.

ISC 2018

Ans :

Osmotic pressure depends only on the number of solute particles present in a solution and not on the chemical nature of the solute. If the number of particles increases, osmotic pressure also increases proportionally. Therefore it behaves similarly to other colligative properties such as boiling point elevation and freezing point depression, which also depend only on particle concentration.

78. Two aqueous solutions, A and B, are separated by a semipermeable membrane. Water moves from A to B. What can you conclude about the two solutions?

ISC 2020

Ans :

The movement of water from A to B indicates that solution B is more concentrated than solution A. Osmosis always occurs from a region of lower solute concentration to higher solute concentration through a semipermeable membrane. Therefore solution B possesses lower solvent concentration and higher osmotic pressure compared to solution A.

79. Why are saline drips used in hospitals required to be isotonic with blood?

ISC 2011

Ans :

If the saline solution is not isotonic with blood, osmosis may occur across red blood cell membranes. In hypotonic solutions, cells swell and may burst, whereas in hypertonic solutions, cells shrink. Therefore saline solutions used in hospitals are made isotonic with blood to maintain normal cell structure and function.

80. A student observes that pure water freezes at 0°C, but seawater freezes at a lower temperature. Explain the observation.

ISC 2022

Ans :

Sea water contains dissolved salts which act as non-volatile solutes. Presence of these solute

particles lowers the vapour pressure of water and decreases its freezing point. Therefore sea water must be cooled to a temperature below 0°C before freezing begins. This phenomenon is known as depression in freezing point.

81. Explain why pressure cookers reduce cooking time at high altitudes.

ISC 2014, 2009

Ans :

At high altitudes, atmospheric pressure is low and water boils at temperatures below 100°C, slowing cooking. In a pressure cooker, steam pressure increases inside the vessel, raising the boiling point of water. As food cooks at higher temperature, cooking becomes faster and more efficient.

82. Why do electrolyte solutions show larger colligative effects than non-electrolyte solutions of the same concentration?

ISC 2013

Ans :

Electrolytes dissociate into ions when dissolved in water, increasing the total number of solute particles in solution. Non-electrolytes do not dissociate and therefore produce fewer particles. Since colligative properties depend upon number of particles present, electrolyte solutions exhibit greater colligative effects than non-electrolyte solutions.

83. Explain why addition of ethylene glycol to water prevents freezing of car radiators during winter.

ISC 2012

Ans :

Ethylene glycol acts as a non-volatile solute and lowers the freezing point of water. Due to depression in freezing point, radiator water remains liquid even at temperatures below 0°C. This prevents freezing and damage to the engine during extremely cold weather conditions.

84. A concentrated sugar solution and distilled water are separated by a semipermeable membrane. Predict the direction of solvent flow and explain.

ISC 2024, 2003

Ans :

Distilled water contains lower solute concentration than sugar solution. Therefore solvent molecules move from distilled water towards concentrated sugar solution through the semipermeable membrane. This process occurs due to osmotic pressure difference between the two sides and continues until equilibrium is established.

85. Why is glucose solution preferred over distilled water for intravenous injections?

ISC 2021 Semi II

Ans :

Distilled water is hypotonic compared to blood and may cause red blood cells to swell and burst due to osmosis. Glucose solutions are prepared isotonic with blood plasma, preventing damage to blood cells and maintaining proper osmotic balance during intravenous administration.

86. A liquid with strong intermolecular forces possesses lower vapour pressure. Explain.

ISC 2022

Ans :

Strong intermolecular forces hold liquid molecules tightly together and reduce their tendency to escape into vapour phase. As a result, fewer molecules are present in the vapour state at equilibrium, causing the liquid to exhibit lower vapour pressure compared to liquids with weaker intermolecular forces.

87. Why does an aqueous solution of urea not show abnormal molar mass, whereas NaCl solution does?

ISC 2006

Ans :

Urea is a non-electrolyte and does not dissociate or associate in aqueous solution. Therefore it shows normal colligative behaviour and normal molar mass. NaCl dissociates into Na^+ and Cl^- ions, increasing particle number and causing abnormal colligative properties and abnormal molar mass determination.

FOUR MARKS QUESTIONS

88. Explain why osmotic pressure method is preferred for determination of molar masses of proteins and polymers.

ISC 2023

Ans :

Proteins and polymers possess very high molar masses and are often sensitive to heat. Methods based on elevation in boiling point or depression

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in freezing point produce extremely small changes which are difficult to measure accurately.

Osmotic pressure measurements are carried out at room temperature and provide reliable results even for very dilute solutions. Therefore decomposition of biomolecules is avoided and accurate molar masses can be determined.

Hence osmotic pressure method is preferred for proteins, enzymes and polymeric substances.

89. Explain why liquids possessing strong intermolecular forces generally have low vapour pressure and high boiling point.

ISC 2008

Ans :

Intermolecular forces hold molecules together in the liquid state. In liquids having strong intermolecular attractions, molecules are tightly bound and cannot escape easily into vapour phase.

Therefore fewer molecules enter the vapour state and vapour pressure remains low. Since vapour pressure becomes equal to atmospheric pressure only at higher temperature, such liquids possess high boiling points.

For example, water shows strong hydrogen bonding and therefore has lower vapour pressure and higher boiling point compared to many other liquids of similar molecular mass.

90. Explain the significance of Van't Hoff factor in determining molecular behaviour of solutes in solution.

ISC 2006

Ans :

Van't Hoff factor represents the ratio between observed and expected colligative properties. It helps in understanding whether solute particles undergo dissociation or association in solution.

If a solute dissociates into ions, the number of particles increases and Van't Hoff factor becomes greater than one. If solute particles associate to form larger units, the number of particles decreases and Van't Hoff factor becomes less than one.

Thus Van't Hoff factor explains abnormal colligative properties and provides information about molecular behaviour of solutes in solutions.

91. A chemistry student noticed that molarity of a solution changed on heating, whereas molality remained constant. Explain the observation with suitable reasoning.

ISC 2021, 2013

NODIA

Ans :

Molarity is defined as the number of moles of solute present in one litre of solution. Since volume changes with temperature due to thermal expansion or contraction, molarity changes when the solution is heated or cooled.

Molality, however, is defined as the number of moles of solute present in one kilogram of solvent. Mass does not change with temperature, so molality remains constant.

Therefore molality is preferred over molarity in temperature-dependent studies such as colligative property calculations because it gives more accurate and reliable results.

92. During summer season, aquatic organisms often face breathing difficulties in lakes and ponds. Explain the reason using concepts of gas solubility.

ISC 2014

Ans :

Dissolution of gases in liquids is generally an exothermic process. According to Le Chatelier's principle, increase in temperature decreases the solubility of gases in water.

During summer, temperature of lakes and ponds rises considerably, reducing the amount of dissolved oxygen available in water. Aquatic organisms depend on dissolved oxygen for respiration.

As oxygen concentration decreases, aquatic animals experience breathing difficulties and in severe cases may even die due to oxygen deficiency in water bodies.

93. A solution of benzene and acetone shows positive deviation from Raoult's law. Explain the reason and mention its effects on vapour pressure and boiling point.

ISC 2018

Ans :

In benzene–acetone solution, intermolecular attraction between unlike molecules is weaker than the attraction present between molecules of the pure components. Due to weaker A–B interactions, molecules escape more easily into vapour phase.

As a result, vapour pressure of the solution becomes greater than the value predicted by Raoult's law. Since vapour pressure becomes high, the solution boils at a lower temperature than expected.

Such solutions generally show increase in volume and absorption of heat during mixing.

94. Explain why addition of non-volatile solute simultaneously increases boiling point and decreases freezing point of a solvent.

ISC 2022, 2014

Ans :

A non-volatile solute lowers vapour pressure of the solvent because solute particles reduce the escaping tendency of solvent molecules from the liquid surface.

For boiling to occur, vapour pressure must become equal to atmospheric pressure. Since vapour pressure is lowered, higher temperature is required, causing elevation in boiling point.

Similarly, the presence of solute particles interferes with formation of solid crystals during freezing. Therefore lower temperature is needed for freezing, causing depression in freezing point.

95. Explain why carbonated beverages are bottled under high pressure and stored at low temperature.

ISC 2010

Ans :

Carbonated beverages contain dissolved carbon dioxide gas. According to Henry's law, solubility of a gas in a liquid is directly proportional to the pressure of the gas above the liquid. Therefore soft drinks are bottled under high pressure so that a large amount of CO_2 dissolves in the liquid.

Gas solubility also decreases with increase in temperature because dissolution of gases is generally exothermic. Hence soft drinks are stored at low temperature to maintain higher solubility of carbon dioxide.

When the bottle is opened, pressure decreases suddenly and dissolved CO_2 escapes in the form of bubbles and fizz.

96. Explain why electrolyte solutions show abnormal colligative properties whereas non-electrolyte solutions generally do not.

ISC 2021, 2018

Ans :

Colligative properties depend upon the number of solute particles present in solution. Non-electrolytes such as glucose and urea dissolve in water without dissociation, so the number of particles remains unchanged and normal colligative behaviour is observed.

Electrolytes such as NaCl and KCl dissociate into ions in aqueous solution. This increases the total number of particles present in solution beyond the expected value.

As a result, observed colligative properties become larger than normal. Therefore experimentally determined molar masses differ from actual values and are called abnormal molar masses. This behaviour is explained using Van't Hoff factor.

97. Explain the principle of reverse osmosis and discuss its importance in water purification.

ISC 2008

Ans :

In ordinary osmosis, solvent molecules pass through a semipermeable membrane from dilute solution towards concentrated solution. Reverse osmosis is the reverse process in which external pressure greater than osmotic pressure is applied on the concentrated solution side.

Due to this high pressure, solvent molecules are forced to move from solution side to pure solvent side through the semipermeable membrane, while dissolved salts and impurities remain behind.

This principle is widely used in purification of drinking water and desalination of sea water. Reverse osmosis plants are extensively used in coastal regions and domestic water purifiers to obtain clean and safe water for consumption.

98. A student prepared two aqueous solutions of equal concentration — one containing glucose and the other containing sodium chloride. The sodium chloride solution showed greater boiling point elevation. Explain the observation in detail.

ISC 2024

Ans :

Glucose is a non-electrolyte and does not dissociate into ions when dissolved in water. Therefore each glucose molecule remains as a single particle in solution. Sodium chloride, however, is an electrolyte and dissociates into Na^+ and Cl^- ions in aqueous solution.

As a result, one formula unit of NaCl produces two particles in solution. Since elevation in boiling point is a colligative property, it depends only upon the number of solute particles present and not upon their chemical nature.

Because NaCl produces greater number of particles than glucose at the same concentration, the lowering of vapour pressure is greater. Hence the boiling point of NaCl solution increases more than that of glucose solution.

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99. During an experiment, a student observed that a mixture of acetone and chloroform possessed lower vapour pressure than expected from Raoult's law. Explain the reason and discuss the nature of the solution formed.

ISC 2022

Ans :

Acetone and chloroform form strong intermolecular hydrogen bonds between unlike molecules. The hydrogen atom of chloroform interacts strongly with the oxygen atom of acetone. These A–B intermolecular attractions become stronger than the attractions present in the pure liquids.

Due to these strong intermolecular forces, the escaping tendency of molecules from the liquid surface decreases significantly. Consequently, fewer molecules enter the vapour phase and vapour pressure becomes lower than the value predicted by Raoult's law.

Therefore the solution shows negative deviation from Raoult's law. Such solutions generally show increase in boiling point, decrease in vapour pressure and contraction in volume during mixing.

100. Distinguish between ideal and non-ideal solutions with respect to intermolecular interactions, thermodynamic properties and vapour pressure behaviour.

ISC 2011

Ans :

Ideal solutions are those solutions in which intermolecular attractions between unlike molecules are nearly equal to those between like molecules. Therefore such solutions obey Raoult's law throughout the concentration range.

For ideal solutions:

- $\Delta H_{mix} = 0$
- $\Delta V_{mix} = 0$
- No heat is evolved or absorbed during mixing.

Examples include benzene and toluene.

Non-ideal solutions are those in which intermolecular attractions between unlike molecules differ significantly from those between like molecules. Hence these solutions do not obey Raoult's law.

For non-ideal solutions:

- $\Delta H_{mix} \neq 0$
- $\Delta V_{mix} \neq 0$
- Vapour pressure deviates from ideal behaviour.

Examples include acetone and chloroform.

101. A student observed that sea water freezes at a much lower temperature than pure water. Explain the observation on the basis of colligative properties.

ISC 2025

Ans :

Sea water contains large amounts of dissolved salts such as sodium chloride and magnesium salts. These dissolved substances behave as non-volatile solutes and lower the vapour pressure of water.

When solute particles are present, they interfere with the arrangement of water molecules into a solid crystalline structure. Therefore lower temperature is required for freezing to occur.

This lowering of freezing point due to presence of solute particles is called depression in freezing point. Since it depends only on number of dissolved particles and not on their nature, it is classified as a colligative property.

Hence sea water freezes at a temperature lower than 0°C, whereas pure water freezes exactly at 0°C.

102. A patient is given glucose drip instead of pure water during intravenous injection. Explain the scientific reason behind this practice.

ISC 2023

Ans :

Pure water is hypotonic compared to blood plasma. If pure water is injected directly into blood, water molecules enter red blood cells through osmosis. This causes swelling and bursting of blood cells, a process known as haemolysis.

Glucose solution used in intravenous injections is prepared isotonic with blood plasma. Therefore osmotic pressure inside and outside the blood cells remains balanced and no net movement of water occurs.

As a result, blood cells remain normal and body fluids maintain proper osmotic balance during medical treatment.

NODIA

NUMERICAL QUESTIONS

103. If 1.71 g of sugar (molar mass = 342 g/mol) are dissolved in 500 mL of an aqueous solution at 300 K, what will be its osmotic pressure?

ISC 2015

Ans :

Given, Weight of sugar $= 1.71$ g

Molar mass of sugar $= 342$ g/mol

Volume of solvent $= 500$ mL

Temperature $= 300$ K

Osmotic pressure, $\pi = CRT$

$$C = \frac{1.71}{342} \times \frac{1000}{500}$$

$$\pi = 0.01 \times 0.821\,\text{L atm/K/mol} \times 300\,\text{K}$$

$$C = 0.01\,\text{mol/L},\ \pi = 0.2463\,\text{atm}$$

104. 0.70 g of an organic compound when dissolved in 32 g of acetone produces an elevation of 0.25° C in the boiling point. Calculate the molecular mass of organic compound.
(K_b for acetone $= 1.72\,\text{K kg mol}^{-1}$)

ISC 2015

Ans :

Given,

$$\Delta T_b = 0.25^\circ, \text{ or } 0.25\text{ K},$$

$$K_b = 1.72\,\text{kg mol}^{-1}$$

$$\Delta T_b = K_b \times m$$

$$0.25 = 1.72 \times \frac{0.70}{\text{molecular weight}} \times \frac{1000}{32\,\text{g}}$$

Molecular weight $= 150.5$ g

105. The osmotic pressure of 20 g haemoglobin in 500 mL of solution is 0.016 atm at 25° C. Calculate the molecular mass of haemoglobin.

ISC Specimen 2023

Ans :

Osmotic pressure (π) is given by

$$\pi = CRT = \frac{nRT}{V} \qquad \left(n = \frac{W}{M}\right)$$

$$= \frac{WRT}{MV}$$

Given, $\pi = 0.016$ atm, $V = 500$ mL,

$$T = 25^\circ\text{C} = 298\,\text{K}$$

$$0.016 = \frac{20 \times 0.0821 \times 298 \times 1000}{M \times 500}$$

$$M = 611645\,\text{g/mol}$$

106. A solution of urea in water has boiling point 100.128° C. Calculate the freezing point of the same solution. Molal constants for water are $K_b = 0.512\,\text{K kg mol}^{-1}$ and $K_f = 1.86\,\text{K kg mol}^{-1}$ respectively.

ISC Specimen 2023

Ans :

Boiling point of solution $= 100.128^\circ$ C

$$K_b = 0.512\,\text{K kg mol}^{-1}$$

$$K_f = 1.86\,\text{K kg mol}^{-1}$$

$$\Delta T_b = 100.128^\circ\text{C} - 100^\circ\text{C}$$

$$= 0.128^\circ\text{C}$$

$$\Delta T_b = K_b \times \text{molality}$$

$$\text{Molality} = \frac{0.128}{0.512} = 0.25$$

Now, $\Delta T_{\text{freezing}} = K_f \times \text{molality}$

$$= 1.86 \times 0.25 = 0.465$$

Freezing point of solution $= 0 - 0.46 = -0.46^\circ$ C

107. Calculate the mass of ascorbic acid (molecular mass =176 g/mol) that should be dissolved in 155 g of acetic acid to cause a depression of freeing point by 1.15 K. Assume that ascorbic acid does not dissociate or associate in the solution.
[K_f for acetic acid = 3.9 K kg/mol]

ISC 2023

Ans :

Given,

W_1, Mass of acetic acid = 155 g

M_2, Molecular mass of $(C_6H_8O_6) = 176$ g/mol

Depression of freezing point = 1.15 K

We know,

$$\Delta T_f = \frac{K_f \times 1000 \times w_2}{M_2 \times W_1}$$

$$1.15 = \frac{3.9 \times 1000 \times w_2}{176 \times 155}$$

$$w_2 = \frac{176 \times 155 \times 1.15}{3.9 \times 1000} = 8.04\,\text{g}$$

108. A 2 molal solution of sodium chloride in water causes an elevation in the boiling point of water by 1.88 K. What is the value of van't Hoff factor? What does it signify?
($K_b = 0.52\text{K kg mol}^{-1}$)

ISC 2014

Ans :

Given, Molality, $m = 2$,

Elevation in boiling point,

$$\Delta T_b = 1.88\,\text{K},$$

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Van't Hoff factor, $i = ?$,

$K_b = 0.52\,\text{K kg mol}^{-1}$

We know that, $\Delta T_b = iK_b m$

Van't Hoff factor, $i = \Delta T_b / K_b \times m$

$$= \frac{1.88}{0.52 \times 2} = 1.807$$

Since, value of Van't Hoff factor is greater than one, it signifies that solute undergoes dissociation.

109. Calculate the mass of compound (molar mass $= 256\,\text{g mol}^{-1}$) to be dissolved in 75 g of benzene to lower its freezing point by 0.48 K.
($K_f = 5.12\,\text{K kg mol}^{-1}$).

ISC Specimen 2018

Ans :

Given that, $K_f = 5.12\,\text{K kg mol}^{-1}$

Mass of benzene, $W_1 = 75\,\text{g}$

Depression in freezing point,

$$\Delta T_f = 0.48\,\text{K}$$

Molar mass of compound,

$$M_2 = 256\,\text{g mol}^{-1}$$

If w_2 is the mass of compound,

Then, $$\Delta T_f = \frac{K_f \times w_2 \times 1000}{W_1 \times M_2}$$

$$0.48 = \frac{5.12 \times w_2 \times 1000}{75 \times 256}$$

$$w_2 = \frac{0.48 \times 75 \times 256}{5.12 \times 1000} = 1.8\,\text{g}$$

110. Calculate the osmotic pressure of a solution prepared by dissolving 0.025 g of K_2SO_4 in 2.0 litres of water at 25°C.
Assuming that K_2SO_4 is completely dissociated (molecular weight of $K_2SO_4 = 174\,\text{g mol}^{-1}$).

ISC 2024

Ans :

By using formula $\pi = CRT$, we can calculate the value of osmotic pressure (π).

Given, mass of $K_2SO_4 = 0.025\,\text{g}$

Molar mass of $K_2SO_4 = 174\,\text{g mol}^{-1}$

Number of moles of solute dissolved (n)

$$= \frac{0.025\,\text{g}}{174\,\text{g mol}^{-1}} = \frac{0.025}{174}\,\text{mol},$$

$V = 2L$

$T = 25^\circ C = 25 + 273 = 298\,\text{K}$

$R = 8.314\,\text{kPa L K}^{-1}\,\text{mol}^{-1}$

$= 8.314 \times 10^3\,\text{Pa LK}^{-1}\,\text{mol}^{-1}$

Substituting these values, in formula $\pi = \frac{n}{V}RT$, we get,

$\pi = \frac{0.025}{174}\,\text{mol} \times \frac{1}{2\text{L}} \times 8.314 \times 10^3\,\text{Pa LK}^{-1}\text{mol}^{-1} \times 298\,\text{K}$

$\pi = 177.98\,\text{Pa}$

111. If the molality of an aqueous solution of cane sugar is 0.4445, what is the mole fraction of cane sugar?

ISC 2008

Ans :

Molality of cane sugar solution

$$= 0.4445\ \text{mol/kg}$$

That means, number of moles (n) of cane sugar present in 1 kg of water = 0.4445

We know that, number of moles of water,

$$(N) = \frac{1000}{18} = 55.5555$$

Density of water = 1000 kg/m^3 = 1 g/cm ^{3}, molecular weight of H_2O =18 g mol^{-1})

Thus molarity $= \frac{\text{Number of moles of water}}{\text{Volume}(L)}$

$$= \frac{1000/18}{1} = 55.5555\,\text{M}$$

Mole fraction of cane sugar

$$= \frac{n_{\text{solute}}}{n_{\text{solute}} + N_{\text{solvent}}} = \frac{n}{n+N}$$

$$= \frac{0.4445}{0.4445 + 55.5555}$$

$$= \frac{0.4445}{56} = 0.0079$$

112. The osmotic pressure of blood at 37°C is 8.21 atm. How much glucose in grams should be used per litre of aqueous solution for an intravenous injection so that it is isotonic with blood? (Molecular wt. of glucose = 180 g/mol)

ISC 2023

Ans :

Given, $\pi_{\text{blood}} = 8.21\,\text{atm}$, $V = 1\,\text{L}$,

$T = 37 + 273 = 310\,\text{K}$

Blood and glucose are isotonic,

So, both will have same osmotic pressure,

We know, $\pi = CRT$

$$\pi = \frac{n}{V}RT$$

$$\pi V = nRT$$

$$n = \frac{\pi V}{RT}$$

$$n = \frac{8.21 \times 1.0}{0.0821 \times 310} = \frac{10}{31}$$

NODIA

$$\text{Weight of glucose} = n \times \text{molecular weight}$$
$$= \frac{10}{31} \times 180 = 58.064 \text{ g}$$

113. 46 g of ethyl alcohol is dissolved in 18 g of water. Calculate the mole fraction of ethyl alcohol. (Atomic weight of C = 12 , O = 16 and H = 1)
ISC 2011

Ans :

Mass of ethyl alcohol $(w) = 46$ g,

Mass of water $(W) = 18$ g

Molecular weight of ethyl alcohol (C_2H_5OH)

$$= 2 \times 12 + 5 \times 1 + 16 + 1 = 46$$

Number of moles of ethyl alcohol in 46 g

$$= \frac{\text{Mass of ethyl alcohol}}{\text{Molar mass of ethyl alcohol}} = \frac{46}{46} = 1 \text{ mol}$$

Molecular weight of water (H_2O)

$$= 2 \times 1 + 16 = 18$$

Number of moles of water in

$$18 \text{ g} = \frac{18}{18} = 1 \text{ mol}$$

Mole fraction of ethyl alcohol

$$= \frac{{}^{n}C_2H_5OH}{{}^{n}C_2H_5OH + {}^{n}H_2O} = \frac{1}{1+1} = \frac{1}{2} = 0.5$$

114. The boiling point of pure water is 373 K. Calculate the boiling point of an aqueous solution containing 18 g of glucose $(W = 180)$ in 100 g of water. Molal elevation constant of water is $0.52 \text{ K kg mol}^{-1}$.
ISC 2009

Ans :

Given, boiling point of pure water = 373 K

Weight of solute, $w = 18 \text{ g}$,

Weight of solvent, $W = 100 \text{ g}$,

Molecular weight of solute,

$$m = 180 \text{ g mol}^{-1}$$

K_b for water $= 0.52 \text{ K kg mol}^{-1}$

For glucose as solute $i = 1$

$$\Delta T_b = \frac{1000 \times K_b \times w}{m \times W}$$
$$= \frac{1000 \times 0.52 \times 18}{180 \times 100} = 0.52 \text{ K}$$

Boiling point of solution $= T_b + \Delta T_b$

(where, T_b is boiling point of water $= 100^\circ \text{C} = 373 \text{ K}$)

$$= 373 + 0.52 = 373.52 \text{ K}$$

115. What will be the vapour pressure of a solution containing 5 moles of sucrose $(C_{12}H_{22}O_{11})$ in 1 kg of water, if the vapour pressure of pure water is 4.57 rum of Hg ? (C = 12, H = 1, O = 16)
ISC 2014

Ans :

Given, number of moles of sucrose $(n) = 5$ mol

Mass of solvent (water) = 1 kg

Vapour pressure of pure water $(p^\circ) = 4.57$ mm of Hg

Vapour pressure of solution $(p) = ?$

According to Raoult's law,

$$\frac{p^\circ - p}{p^\circ} = \frac{n}{n+N}$$

(where, N is number of moles of water)

$$\frac{4.57 - p}{4.57} = \frac{5}{5 + 55.5} \quad \text{as } N = \frac{1000}{18} = 55.5 \text{ mol})$$

$$4.57 - p = \frac{4.57 \times 5}{60.5} = 0.377$$

$$p = 4.57 - 0.377 = 4.193 \text{ mm of Hg}$$

116. Determine the osmotic pressure of a solution prepared by dissolving 0.025 g of K_2SO_4 in 2 litres of water at 25° C, assuming that K_2SO_4 is completely dissociated. $(R = 0.0821 \text{ L atm K}^{-1}\text{mol}^{-1}$, mol. wt. of $K_2SO_4 = 174 \text{ g mol}^{-1})$.
ISC 2025

Ans :

Given, mass of

$$K_2SO_4(W) = 25 \text{ mg} = 0.025 \text{ g};$$

$$\text{volume } (V) = 2L, \ T = 298 \text{ K}.$$

The reaction of dissociation of K_2SO_4.

$$K_2SO_4 \longrightarrow 2K^+ + SO_4^{2-}$$

Number of ions produced $i = 2 + 1 = 3$

as $$\pi = i\frac{n}{V}RT = i\frac{W}{MV}RT$$

where, $R = 0.082 \text{ L atmK}^{-1}\text{mol}^{-1}$, molar mass of

$$K_2SO_4 = 174 \text{ g/mol}$$

By substituting the value we get

$$T_1 = \frac{3 \times 0.025}{174 \times 2} \times 0.0821 \times 298$$

$$= 5.27 \times 10^{-2} \text{ atm}$$

117. A solution containing 1.23 g of calcium nitrate in 10 g of water, boils at 100.975° C at 760 mm of Hg. Calculate the van't Hoff factor for the salt at this concentration. (K_b for water $= 0.52 \text{ K kg mol}^{-1}$, molecular weight of calcium nitrate $= 164 \text{ g mol}^{-1}$)
ISC 2020

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Ans :

Given, mass of calcium nitrate = 1.23 g

$$\text{Mass of water} = 10\text{ g}$$

$$T_b \text{ for solution} = 100.975^\circ\text{C}$$

$$K_b \text{ for water} = 0.52\text{ K kg mol}^{-1}$$

Molecular weight of calcium nitrate = 164 g mol^{-1}

$$\Delta T_b = i \times K_b \times m$$

$$\Delta T_b = i \times K_b \times \frac{w_B}{M_B} \times \frac{1000}{W_A}$$

$$100.975 - 100^\circ\text{C} = i \times 0.52 \times \frac{1.23}{164} \times \frac{1000}{10}$$

or $$0.975 = i \times 0.52 \times 0.75$$

$$i = 2.5$$

118. Determine the freezing point of a solution containing 0.625 g of glucose ($C_6H_{12}O_6$) dissolved in 102.8 g of water. (Freezing point of water = 273 K, K_f for water = 1.87 K kg mol^{-1}, at. wt. of C = 12, H = 1 and O = 16)

ISC 2017

Ans :

Given, Freezing point of water = 273 K

Weight of solute (glucose) $w = 0.625$ g

Weight of solvent, $W = 102.8$ g

Molecular weight of solute,

$$m = (C_6H_{12}O_6)$$

$$= 12 \times 6 + 1 \times 12 + 16 \times 6$$

$$= 180\text{ g mol}^{-1}$$

$$K_f \text{ for water} = 1.87\text{ K kg mol}^{-1}$$

For glucose as solute, $i = 1$

$$\Delta T_f = \frac{1000 \times K_f \times w}{m \times W}$$

$$= \frac{1000 \times 1.87 \times 0.625}{180 \times 102.8}$$

$$= 0.063\text{ K}$$

Freezing point of solution = $T_f + \Delta T_f$

(where, T_f is freezing point of water = 0° C = 273 K

$$= 273 + 0.063 = 273.063\text{ K}$$

119. The molecular weight of an organic compound is 58 g mol^{-1}. What will be the boiling point of a solution containing 48 g of the solute in 1200 g of water?

ISC 2016

Ans :

Given,

$W_a =$ Weight of H_2O (solvent) = 1200 g

$w_b =$ Weight of organic compound = 48 g

$T_b^o = 100^\circ\text{C}$, $K_b = 0.513^\circ\text{C kg mol}^{-1}$

$$\Delta T_b = \frac{K_b \times 1000 \times w_b}{M_b \times W_a}$$

$$= \frac{(0.513^\circ\text{C kg mol}^{-1}) \times 100 \times 48\text{ g}}{(58\text{ g mol}^{-1}) \times 1200\text{ g}}$$

$$= 0.0353^\circ\text{C}$$

As we know that,

$$\Delta T_b = T_b - T_b^o$$

$$0.0353 = T_b - 100$$

$$T_b = 100 + 0.0353$$

$$= 100.0353^\circ\text{C} = 373.1853\text{ K}$$

120. A solution containing 0.5 g of KCl dissolves in 100 g of water and freezes at −0.24° C. Calculate the degree of dissociation of the salt. (K_f for water = 1.86° C). (Atomic weights of K = 39, Cl = 35.5).

ISC 2015

Ans :

Given, Weight of KCl (solute) = 0.5 g

Weight of solvent (water) = 100 g

Freezing point (T_f) = − 0.24° C

$K_f = 1.86^\circ\text{C}$

Molecular mass of KCl = 39 + 35.5 = 74.5

From depression in freezing point

$$T_f = i \times K_f \times m$$

$$0.24^\circ\text{C} = i \times 1.86^\circ\text{C} \times \frac{0.5}{74.5} \times \frac{1000}{100}$$

$$i = 1.92$$

For KCl, $i = 1 + \alpha$

(where α is the degree of dissociation)

$$\alpha = 1.92 - 1$$

$$\alpha = .92 \text{ or } 92\%$$

121. Equal weights of two substances X and Y are dissolved in equal volumes of water. The osmotic pressure of the solution containing Y is five times the osmotic pressure of the solution containing X. What is the molecular weight of X if that of Y is 60 ?

ISC 2009

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Ans :

Suppose weight of X and Y are w g and volume of water for each solution $= V$

If π is osmotic pressure of solution containing X, then osmotic pressure of Y is 5 times the solution containing X i.e. 5π.

Now, for solution containing X,

$$\pi = \frac{wRT}{mV} \quad \text{...(i)}$$

For solution containing Y,

$$5\pi = \frac{wRT}{60\,\text{V}} \text{ (As, } m \text{ for } Y = 60) \quad \text{...(ii)}$$

On dividing Eq. (i) by Eq. (ii), we get

$$\frac{\pi}{5\pi} = \frac{wRT \times 60\,\text{V}}{mV \times wRT}$$

$$\frac{1}{5} = \frac{60}{m}$$

$$m = 300$$

Therefore, molecular weight of $X = 300\,\text{gmol}^{-1}$

122. Ethylene glycol is used as an antifreeze agent. Calculate the amount of ethylene glycol to be added to 4 kg of water to prevent it from freezing at $-6^\circ\,\text{C}$.

(K_f for $H_2O = 1.85\,\text{K mol}^{-1}\text{kg}$)

ISC 2024

Ans :

Given, mass of water $(W) = 4\,\text{kg}$,

$$K_f = 1.85\,\text{K kg mol}^{-1}$$

$$\Delta T_f = 0 - (-6) = 6^\circ\,\text{C}$$

(as, freezing point of pure water is $0^\circ\,\text{C}$).

Mass of ethylene glycol $(w) = ?$

Molar mass of ethylene glycol

$[\text{CH}_2\text{OH} \cdot \text{CH}_2\text{OH}]$, $M' = 62\,\text{g mol}^{-1}$

We know that,

$$\Delta T_f = \frac{K_f \times w}{M' \times W(\text{kg})}$$

$$w = \frac{\Delta T_f \times M' \times W(\text{kg})}{K_f}$$

$$= \frac{6 \times 62 \times 4}{1.85} = 804.32\,\text{g}$$

123. A solution is prepared by dissolving 9.25 g of non-volatile solute in 450 mL of water. It has an osmotic pressure of 350 mm of Hg at $27^\circ\,\text{C}$. Assuming the solute is non-electrolyte, determine its molecular mass. $(R = 0.0821\,\text{L atm K}^{-1}\,\text{mol}^{-1})$

ISC 2019

Ans :

Given : Mass of non-volatile solute $(w_B) = 9.25\,\text{g}$

Volume of water $(V_A) = 450\,\text{mL}$

Osmotic pressure $(\pi) = \frac{350}{760} = 0.46\,\text{atm}$

Temperature $(T) = 27 + 273 = 300\,\text{K}$

Gas constant $(R) = 0.0821\,\text{L atm K}^{-1}\text{mol}^{-1}$

Now, $\pi = CRT = \frac{w_B \times 1000 \times RT}{M_B \times V}$

M_B [molecular mass of non-volatile solute]

$$= \frac{w_B \times 1000 \times R \times T}{V \times \pi}$$

or $$M_B = \frac{w_B \times 1000 \times R \times T}{V \times \pi}$$

$$= \frac{9.25\,\text{g} \times 1000 \times 0.0821\,\text{L atm K}^{-1}\text{mol}^{-1} \times 300\,\text{K}}{450\,\text{mL} \times 0.46\,\text{atm}}$$

$$M_B = \frac{2278275}{20.7} = 1100.6\,\text{g mol}^{-1}$$

Hence, molecular mass of non-volatile solute

$$= 1100.6\,\text{g mol}^{-1}$$

124. Calculate the amount of $CaCl_2$ (molar mass $= 111\,\text{g mol}^{-1}$) which must be added to 500 g of water to lower its freezing point by 2 K, assuming $CaCl_2$ is completely dissociated. (K_f for water $= 1.86\,\text{K kg mol}^{-1}$).

ISC Specimen 2018

Ans :

Given, $K_f = 1.86\,\text{K kg mol}^{-1}$,

$\Delta T_f = 2\,\text{K}$,

Amount of water taken $(W_1) = 500\,\text{g}$

Amount of $CaCl_2 (w_2) = 0$

Molar mass of $CaCl_2 (M_2) = 111\,\text{g mol}^{-1}$

It is given that $CaCl_2$ is completely dissociated,

$$CaCl_2 \longrightarrow Ca^{2+} + 2Cl^-$$

Number of particles after dissociation $= 3$

Van't Hoff factor,

$$i = 3$$

$$\Delta T_f = \frac{i \times K_f \times w_2 \times 1000}{W_1 \times M_2}$$

$$w_2 = \frac{\Delta T_f \times W_1 \times M_2}{i \times K_f \times 1000}$$

$$= \frac{2 \times 500 \times 111}{3 \times 1.86 \times 1000} = 19.89\,\text{g}$$

NODIA

125. The osmotic pressure of 0.01 molar solution of an electrolyte is found to be 0.65 atm at 27° C. Calculate the van't Hoff factor. What conclusion can you draw about the molecular state of the solute in the solution?

ISC 2011

Ans :

Given, osmotic pressure

$$(\pi_{obs}) = 0.65 \text{ atm}$$

Temperature, $T = 27^\circ \text{C} = (27 + 273)\text{ K} = 300 \text{ K}$

Concentration, $C = 0.01 \text{ M}$

van't Hoff factor, $i = ?$

We know that, $\pi_{cal.} = CRT$

$$= 0.01 \text{ M} \times 0.0821 \text{ L atm K}^{-1} \times 300 \text{ K}$$

$$= 0.2463 \text{ atm}$$

Bur, $\pi_{calc} = 0.65 \text{ atm}$

van't Hoff factor, $i = \frac{\pi_{obs}}{\pi_{cal}} = \frac{0.2463}{0.65} = 0.3789$

i.e. $i < 1$

When, $i < 1$, the solute undergoes association.

Thus, it gets associated in solution.

126. Albumins are the most abundant proteins in blood. At 25° C, 3.5 g of albumin in 100 mL of water produces an osmotic pressure of 0.014 atm. What is the molecular weight of albumin?

ISC 2008

Ans :

We know that, osmotic pressure

$$\pi = CRT = \frac{wRT}{M \times V}$$

or $M = \frac{wRT}{\pi \times V}$

Given, $w = 3.5 \text{ g}$, $R = 0.0821 \text{ dm}^3 \text{ atm K}^{-1}$

$T = 273 + 25 = 298 \text{ K}$, $\pi = 0.014 \text{ atm}$,

$V = 100 \text{ mL}$

Molecular weight of albumin,

$$M = \frac{3.5 \times 0.082 \times 298 \times 1000}{0.014 \times 100}$$

$$= 61090 \text{ g mol}^{-1}$$

Molecular weight of albumin is 61090 g mol^{-1}

127. The osmotic pressure of blood is 7.65 atm at 27° C. How much glucose should be used per litre to prepare an intravenous injection that has the same osmotic pressure as blood?

ISC 2003, 2001

Ans :

Let, the weight of glucose is wg.

If glucose solution has same osmotic pressure as blood.

Thus, $\pi_{glucose} = \pi_{blood} = 7.65 \text{ atm}$

$$\pi = \frac{w \times R \times T}{M \times V}$$

Given : Volume of solution, $V = 1 \text{ L}$

Gas constant, $R = 0.0821 \text{ L atm mol}^{-1}\text{K}^{-1}$

Temperature, $T = 27^\circ \text{C} = (27 + 273)\text{ K}$

$$= 300 \text{ K}$$

Molecular weight of glucose, $M = 180 \text{ g mol}^{-1}$

Thus, $\pi = \frac{w \times 0.0821 \times 300}{180 \times 1}$

$$w = \frac{7.65 \times 180}{0.0821 \times 300}$$

$$= 55.9 \text{ g mol}^{-1}$$

128. 0.5 g of a non-volatile solute is dissolved in 100 g of ethyl acetate at 20° C. The vapour pressure of the solution and pure ethyl acetate are 72.0 torr and 72.8 ton, respectively at −28° C. Calculate molecular weight of the solute.

ISC 2001

Ans :

Given that, weight of solvent, $w = 100 \text{ g}$

Vapour pressure of solution, $p = 72.0 \text{ torr}$

Vapour pressure of solvent (ethyl acetate),

$$p^\circ = 72.8 \text{ torr}$$

Molecular weight of solvent $= 88 \text{ g mol}^{-1}$

According to Raoult's law,

$$\frac{p^\circ - p}{p^\circ} = \frac{n}{N + n}$$

But for dilute solutions, $n <<< N$

Thus, $\frac{p^\circ - p}{p^\circ} = \frac{n}{N}$

$$\frac{72.8 - 72}{72.8} = \frac{0.5/\text{m}}{100/88}$$

$$m = \frac{0.5}{0.8} \times \frac{88}{100} \times 72.8$$

$$= 40.04$$

Hence, molecular weight of non-volatile solute is 40.04 g mol^{-1}.

129. The freezing point of nitrobenzene is 278.8 K. A 0.25 molal solution of a substance (molecular weight = 120) in nitrobenzene has a freezing point of 276.8 K. Calculate the molal depression constant of nitrobenzene.

ISC 2002

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Ans :

Given that, $T_f^o = 278.8\,\text{K}$

Molality of a solution,

$$m = 0.25\,\text{m}$$

$$w = 120\,\text{g mol}^{-1}$$

Freezing point of solution,

$$T_{f'} = 276.8\,\text{K}$$

It is known that, $\Delta T_f = i \times K_f \times m$

$$K_f = \frac{\Delta T_f}{i \times m}$$

Here, van't Hoff factor, i for solute is considered as 1.

Depression in freezing point,

$$\Delta T_f = T_f^o = T_f'$$

$$= 278.8 - 276.8\,\text{K} = 2\,\text{K}$$

$$K_f = \frac{2}{1 \times 0.25} = 8\,\text{K molal}^{-1}$$

130. Calculate osmotic pressure of a solution containing 3.42 g of sucrose in 1 L of water at 400 K.

ISC 2024

Ans :

Given that, weight of sucrose $= 3.42\,\text{g}$

Volume of solution $= 1\,\text{L}$

$$T = 400\,\text{K}$$

Molecular weight of sucrose $= 342\,\text{g mol}^{-1}$

Gas constant, $R = 0.0821\,\text{atm K}^{-1}\text{mol}^{-1}$

Osmotic pressure (π) of a solution is given by

$$\pi = \frac{w \times R \times T}{mV}$$

$$= \frac{3.42 \times 0.0821 \times 400}{342 \times 1}$$

$$= 0.328\,\text{atm} \approx 0.33\,\text{atm}$$

131. The cryoscopic constant of water is $1.86\,\text{K mol}^{-1}\,\text{kg}^{-1}$.An aqueous solution of cane sugar freezes at $-0.372^\circ\,\text{C}$. Calculate molality of the solution.

ISC 2000

Ans :

Given, Cryoscopic constant,

$$K_f = 1.86\,\text{K mol}^{-1}\text{kg}^{-1}$$

Freezing point of solution,

$$T_{f'} = -0.327^\circ\,\text{C}$$

$$= [273 + (-0.327)]\,\text{K}$$

$$= 272.673\,\text{K}$$

Freezing point of pure water,

$$T_f^o = 0^\circ\,\text{C} = 273\,\text{K}$$

Depression in freezing point,

$$\Delta T_f = T_f^o - T_{f'}$$

$$= 273 - 272.673\,\text{K} = 0.327\,\text{K}$$

$$\Delta T_f = i \times K_f \times m$$

Since, cane sugar is a non-electrolyte, thus i(van't Hoff factor) is equal to 1.

$$0.327 = 1 \times 1.86 \times m$$

$$m = \frac{0.327}{1.86}$$

$$= 0.17\,\text{molal} \approx 0.2\,\text{molal}$$

Hence, molality of solution is 0.2 molal.

132. The elevation in boiling point when 0.30 g of acetic acid is dissolved in 100 g of benzene is 0.0633°C. Calculate the molecular weight of acetic acid from this data. What conclusion can you draw about the molecular state of the solute in the solution? (Given K_b for benzene $= 2.53\,\text{K kg mol}^{-1}$, at. wt. of C = 12, H = 1, O = 16).

ISC 2020

Ans :

Given, weight of solute $(w_B) = 0.30\,\text{g}$

Weight of solvent

$$(W_A) = 100\,\text{g}$$

$$\Delta T_b = 0.0633^\circ\,\text{C} = 0.0633\,\text{K}$$

$$K_b = 2.53\,\text{K kg mol}^{-1}$$

$$M_B = \frac{K_b \times w_B \times 1000}{W_A \times \Delta T_b}$$

$$= \frac{2.53 \times 1000 \times 0.30}{100 \times 0.0633} = 119.9\,\text{g/mol}$$

$$i = \frac{\text{Normal molar mass}}{\text{Abnormal molar mass}}$$

$$\frac{60}{119.90} = 0.5$$

$$i < 1$$

As i is less than 1, thus association will take place.

133. Calculate the mole fraction of water in a sodium hydroxide solution which has 80 g of NaOH and 54 g of H_2O. (Relative atomic masses of Na = 23, O = 16 and H = 1)

ISC 2005

Ans :

Molecular mass of NaOH

$$= 23 + 16 + 1 = 40\,\text{gmol}^{-1}$$

NODIA

Number of moles of NaOH in 80 g

$$(n) = \frac{\text{Mass of NaOH}}{\text{Molecular mass of NaOH}}$$

$$= \frac{80}{40} = 2 \text{ mol}$$

Molecular mass of water

$$= 2 + 16 = 18 \text{ gmol}^{-1}$$

Number of moles of water in 54 g,

$$(N) = \frac{54}{18} = 3 \text{ mol}$$

Total number of moles in solution

$$= n + N$$

$$= 2 + 3 = 5 \text{ mol}$$

Mole fraction of water in solution

$$= \frac{\text{Number of moles of water}}{\text{Total number of moles present in solution}}$$

$$= \frac{N}{n+N} = \frac{3}{5} = 0.6$$

134. Calculate the boiling point of urea solution when 6 g of urea is dissolved in 200 g of water.
(K_b for water $= 0.52 \text{ K kg mol}^{-1}$, boiling point of pure water = 373 K, mol. wt. of urea = 60)

ISC 2019

Ans :

Given

Mass of solute (urea), i.e. $w_B = 6 \text{ g}$

Mass of water (solvent), i.e.

$$W_A = 200 \text{ g}$$

Molar mass of urea, $M_B = 60 \text{ g mol}^{-1}$

$$K_f \text{ for water} = 0.52 \text{ K kg mol}^{-1}$$

Boiling point (b.p) of pure water = 373 K

ΔT_b (elevation in b.p.)

$$= K_f \times \frac{w_B}{M_B} \times \frac{1000}{W_A}$$

$$= \frac{0.52 \text{ K kg mol}^{-1} \times 6 \text{ g} \times 1000}{60 \text{ g mol}^{-1} \times 200 \text{ g}}$$

$$\Delta T_b = 0.26^\circ \text{ K}$$

Thus, boiling point of solution,

$$T = T^\circ + \Delta T_b = 373 + 0.26 = 373.26 \text{ K}$$

135. A solution X is prepared by dissolving 3 moles of glucose in one litre of water and a solution Y is prepared by dissolving 1.5 moles of sodium chloride in one litre of water. Will the osmotic pressure of X be higher, lower or equal to that of Y ? Give a reason for your answer.

ISC 2012

Ans :

Osmotic pressure is a colligative property which depends on the number of particles present in solution. Since, glucose is non-electrolyte.

Value of van't Hoff factor i for sodium chloride = 1

and $n = 3$ mol

Value of van't Hoff factor i for sodium chloride = 2

and n =1.5 mol

Now for glucose, osmotic pressure,

$$\pi = \frac{inRT}{V}$$

[Here, volume (V) of water = 1000 mL]

$$= 1 \times 3\, RT/1000 = 3\, RT/100$$

For NaCl, osmotic pressure,

$$\pi = \frac{inRT}{V}$$

$$= 2 \times 1.5\, RT/1000 = 3\, RT/1000$$

π is same for both the solution.

136. The freezing point of a solution containing 0.3 g of acetic acid in 30 g of benzene is lowered by 0.45 K . Calculate the Van't Hoff factor.
(Atomic weight of C = 12, H = 1, O = 16, K_f for benzene $= 5.12 \text{ K kg mol}^{-1}$)

ISC 2013

Ans :

Given, amount of acetic acid

$$(w) = 0.3 \text{ g},$$

Amount of benzene $(W) = 30 \text{ g}$,

Depression in freezing point,

$$\Delta T_f = 0.45 \text{ K},$$

$$K_f = 5.12 \text{ K kg mol}^{-1}$$

We know that, $\Delta T_f = iK_f m$

(where, m is molality and i represents van't Hoff factor)

$$\text{Molality, } m = \frac{w \times 1000}{M' \times W} = \frac{0.3 \times 1000}{60 \times 30}$$

$$= 0.166 \approx 0.17$$

[as molar mass of acetic acid (CH_3COOH)

$$M' = 2 \times 12 + 4 \times 1 + 2 \times 16$$

$$= 60 \text{ g mol}^{-1}$$

Now, $$i = \frac{\Delta T_f}{K_f \times m}$$

$$= \frac{0.45}{5.12 \times 0.17} = 0.517$$

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137. An aqueous solution containing 1.70 g of cane sugar in 100 mL water begins to freeze at -0.093° C. The water is 1.86 kg mol^{-1}. Calculate the molecular cryoscopic constant (molal depression constant) of weight of cane sugar.

ISC 2007

Ans :

We know that, molecular mass

$$= \frac{i \times 1000 \times K_f \times w}{\Delta T \times W(g)}$$

For cane sugar $i = 1$,

w(cane sugar) $= 1.70$ g

$W = 100$ g water

$\Delta T = 0 - (-0.093) = 0.093$

$K_f = 1.86$ K kg mol^{-1}

$$\text{Molecular mass} = \frac{1 \times 1000 \times 1.86 \times 1.7}{0.093 \times 100}$$

$$= 340 \text{ g mol}^{-1}$$

138. A decinormal solution of sodium chloride exerts an osmotic pressure of 4.82 atm at 27° C. Calculate the degree of dissociation of sodium chloride.

ISC 2007

Ans :

Equivalent weight of NaCl

= Molecular weight of NaCl

0.1 N NaCl = 0.1 M NaCl

If NaCl does not dissociate in aqueous solution then for a given solution, it is given that,

$C = 0.1$ M, $T = 300$ K$(27 + 273)$

$\pi = CRT$

$= 0.1 \text{ M} \times 0.082 \text{ L atm K}^{-1}\text{mol}^{-1} \times 300 \text{ K}$

$= 2.46$ atm

But observed

$\pi = 4.82$ atm

Van't Hoff factor,

$$i = \frac{\text{Observed magnitude of } \pi}{\text{Normal magnitude of } \pi}$$

$$= \frac{4082}{2046} = 1.95 \approx 2$$

If degree of dissociation is α, then

For NaCl, $m = 2$ as the number of solute particles formed in its aqueous solution is almost double the number of NaCl molecules.

$$\alpha = \frac{i-1}{m-1} = \frac{2-1}{2-1} = 1 \text{ or } 100\%$$

139. The depression in the freezing point of a sugar was found to be 0.402° C. Calculate pressure of the sugar solution at 27° C. ($K_f = 1.86$ K kg mol^{-1}).

ISC 2007

Ans :

Sugar is a non-electrolyte. Therefore, for sugar solution, depression in freezing point takes place.

Given that, $\Delta T_f = 0.402^\circ$ C

$K_f = 1.86$ K kg mol^{-1}

$T = 27 + 273 = 300$ K

$\Delta T_f = m \times K_f$

or $m = \frac{\Delta T_f}{K_f}$

$$= \frac{0.402}{1.86} = 0.216 \text{ mol kg}^{-1}$$

Now, for same solution.

Osmotic pressure, $\pi = CRT$

$= m \times R \times T$

$= 0.216 \times 0.0821 \times 300$

$= 5.32$ atm

140. An aqueous solution containing 0.2 g of compound A in 21.7 g of water freezes at 272.914 K. If the value of K_f for water is 1.86 K kg mol^{-1}, calculate molecular weight of compound A.

ISC 2004

Ans :

Given, $w = 0.2$ g, $W = 21.7$ g

$T_{f'} = 272.914$ K

$K_f = 1.86$ K kg mol^{-1}

$\Delta T_f = T_f - T_{f'}$

$= 273 - 272.914$

(T_f of water $= 0^\circ$ C $= 273$ K)

$= 0.086$ K

If the compound A is non-electrolyte, then $i = 1$.

Now, $\Delta T_f = i \times K_f \times \frac{w \times 1000}{W \times M'}$

$M' = i \times K_f \times \frac{w \times 1000}{W \times \Delta T_f}$

$= 1 \times 1.86 \times \frac{0.2 \times 1000}{21.7 \times 0.086}$

$= 199.33 \text{ g mol}^{-1}$

NODIA

141. An aqueous solution containing 12.48 g of barium chloride in 1000 g of water boils at 373.0832 K. Calculate the degree of dissociation (α) of barium chloride.

K_b for $H_2O = 0.52\ K\ kg\ mol^{-1}$, molecular mass of $BaCl_2 = 208.34\ g\ mol^{-1}$

ISC Specimen 2023

Ans :

Given, boiling point of water $= 373.0832\ K$

Actual boiling point of water $= 373\ K$

$$\Delta T = 373.0832 - 373$$

$$= 0.0832$$

$$\text{Moles of } BaCl_2 = \frac{\text{Given mass}}{\text{Molar mass}} = \frac{12.48}{208.34} = 0.06$$

$$\Delta T_b = K_b \times m \times i$$

($i =$ van't Hoff factor)

$$0.0832 = 0.52 \times 0.06 \times i$$

$$i = \frac{0.0832}{0.52 \times 0.06} = 2.67$$

$$1 + (n-1) \times \alpha = 2.67 \quad \text{(degree of dissociation)}$$

$$1 + 2\alpha = 2.67$$

$$2\alpha = 1.67$$

$$\alpha = 0.835$$

142. A 10% aqueous solution of cane sugar (mol.wt. = 342) is isotonic with 1.754% aqueous solution of urea. Find the molecular mass of urea.[K_b for water $= 0.513^\circ C\ kg\ mol^{-1}$; boiling point of water $=100°C$]

ISC 2016

Ans :

Isotonic solutions have same osmotic pressure at same temperature.

Here, $W_1 =$ weight of cane sugar solution $= 10\ g$

$M_1 =$ molecular weight of cane sugar $= 342\ g$

$w_2 =$ weight of urea solution $= 1.754\ g$

$$\pi = CRT = \frac{w}{m}\frac{RT}{V}$$

For cane sugar and urea solution, π, R, T and V are same.

For cane sugar solution,

$$\pi = \frac{10RT}{342\,V}$$

For urea solution, $\pi = \dfrac{1.754RT}{MV}$

$$\frac{10RT}{342\,V} = \frac{1.754RT}{MV}$$

$$M = \frac{1.754 \times 342}{10} = 59.98\ g$$

143. An aqueous solution containing 12.48 g of barium chloride $(BaCl_2)$ in 1000 g of water, boils at $100.0832^\circ C$. Calculate the degree of dissociation of barium chloride. (K_b for water $= 0.52\ kg\ mol^{-1}$, atomic weight Ba = 137, Cl = 35.5)

ISC 2018

Ans :

Given, $W_2 = 12.48\ g$, $W_1 = 1000\ g$,

$T_{b(\text{solution})} = (100.0832 + 273)\ K = 373.0832\ K$

K_b for $H_2O = 0.52\ kg\ mol^{-1}$

and $M_{2(BaCl_2)} = 208\ g\ mol^{-1}$

$\Delta T_b = T_b - T_b^o$

$= 373.0832\ K - 373\ K = 0.0832\ K$

$$M_{2(\text{Observed})} = \frac{K_b \times w_2 \times 1000}{\Delta T_b \times W_1}$$

$$= \frac{0.52\ kg\ mol^{-1} \times 12.48\ g \times 1000}{0.0832\ K \times 1000\ g}$$

$$M_{2(\text{Observed})} = 78\ g\ mol^{-1}$$

$$i = \frac{M_{2(\text{Calculated})}}{M_{2(\text{Observed})}} = \frac{208\ g\ mol^{-1}}{78\ g\ mol^{-1}} = 2.67$$

For $BaCl_2$, $m = 3$ as it gives 3 ions on dissociation

$$\alpha = \frac{i-1}{m-1}$$

$$= \frac{2.67 - 1}{3 - 1} = \frac{1.67}{2} = 0.835$$

$$\alpha = 83.5\%$$

144. A solution of lactose containing 8.45 g of lactose in 100 g of water has a vapour pressure of 4.559 mm of Hg at 0° C. If the vapour pressure of pure water is 4.579 mm of Hg, calculate the molecular weight of lactose.

ISC 2012

Ans :

Given, vapour pressure of pure water

$(p^\circ) = 4.579\ mm$ of Hg

Vapour pressure of solution

$(p) = 4.559\ mm$ of Hg

Mass of lactose $(w) = 8.45\ g$

Mass of water $(W) = 100\ g$

Molecular mass of $H_2O\ (M) = 18\ g$

Molecular mass of lactose $(m) = ?$

According to Raoult's law,

$$\frac{p^\circ - p}{p^\circ} = \frac{wM}{W \cdot m}$$

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$$\frac{4.579-4.559}{4.579} = \frac{8.45\times 18}{100\times m}$$

$$m = \frac{8.45\times 18\times 4.579}{100\times 0.02}$$

$$= 348.232\ \text{g mol}^{-1}$$

145. What is the mass of a non-volatile solute (molar mass 60) that needs to be dissolved in 100 g of water in order to decrease the vapour pressure of water by 25%? What will be the molality of the solution?

ISC 2010

Ans :

According to Raoult's law, We can write the following equations

$$\frac{\Delta p}{p^\circ} = \frac{p^\circ - p}{p^\circ} = \frac{n}{n+N}$$

$$= \frac{w/m}{w/m + W/M}$$

Given, $\Delta p = 25\%$ (atm), i.e. $p^\circ = 100$ (atm),

$m = 60$, $W = 100$ g,

$M = 18$ (for water), $w = ?$

$$\frac{25}{100} = \frac{w/60}{w/60 + 100/18}$$

$$\frac{1}{4} = \frac{w/60}{\frac{18w + 60\times 100}{18\times 60}}$$

$$w = 111.11\ \text{g}$$

Mass of solute required is 111.11 g.

Now, Molality (m)

$$= \frac{\text{Number of moles of solute}}{\text{Mass of solvent in kg}}$$

$$= \frac{111.11/60}{100/1000} = 18.518$$

146. The freezing point of a solution containing 5.85 g of NaCl in 100 g of water is -3.348° C. Calculate van't Hoff factor 'i' for this solution. What will be the experimental molecular weight of NaCl ? (K_f for water $= 1.86$ K kg mol^{-1}, atomic weight of Na $= 32$, Cl $= 35.5$)

ISC 2018

Ans :

Given, $w_2 = 5.85$ g, $W_1 = 100$ g

$m_1 = 18\ \text{g mol}^{-1}$ for H_2O

Depression in freezing point

$$(\Delta T_f) = T_f^o - T_f$$

$$\Delta T_f = 0^\circ\text{C} - (-3.348)^\circ\text{C}$$

$$= 3.348^\circ\text{C} = 3.348\ \text{K}$$

$$M_2 = \frac{1000\times K_f \times w_2}{\Delta T_f \times W_1}$$

$$M_2 = \frac{1000\times 1.86\ \text{K kg mol}^{-1}\times 5.85\ \text{g}}{3.348\ \text{K}\times 100\ \text{g}}$$

$$= 32.5\ \text{g mol}^{-1}$$

Calculated molecular mass of NaCl

$$= 23 + 35.5 = 58.5\ \text{g mol}^{-1}$$

Now, $i = \frac{\text{Calculated molecular mass}}{\text{Observed molecular mass}}$

$$i = \frac{58.5}{32.5} = 1.8$$

van't Hoff factor $(i) = 1.8$

147. A solution containing 0.5 g of KCl dissolves in 100 g of water and freezes at -0.24° C. Calculate the degree of dissociation of the salt. (K_f for water $= 1.86^\circ$ C).

ISC Specimen 2018

Ans :

Given, K_f for water $= 1.86^\circ$ C

Amount of KCl taken $(w_2) = 0.5$ g

Amount of water taken $(W_1) = 100$ g

$$\Delta T_f = 0 - (-0.24)$$

$$= 0.24^\circ\text{C}$$

Observe molecular mass of

$$\text{KCl}(M_2) = \frac{1000\times K_f \times w_2}{\Delta T_f \times W_1}$$

$$= \frac{1000\times 1.86\times 0.5}{0.24\times 100}$$

$$= 38.75\ \text{g mol}^{-1}$$

Normal molecular mass of

$$\text{KCl} = 39 + 35.5$$

$$= 74.5\ \text{g mol}^{-1}$$

$$\text{van't Hoff factor} = \frac{\text{Normal molecular mass}}{\text{Observed molecular mass}}$$

$$i = \frac{74.5}{38.75} = 1.92$$

$$\text{KCl} \rightleftharpoons \text{K}^+ + \text{Cl}^-$$

Initial moles	1 mol	0	0
Moles after dissociation	$1-\alpha$	α	α

Total number of moles after dissociation

$$= 1 - \alpha + \alpha + \alpha = 1 + \alpha$$

$$i = 1 + \alpha$$

$$1.92 = 1 + \alpha$$

So, degree of dissociation, $\alpha = 1.92 - 1 = 0.92$, i.e. 92% dissociated.

NODIA

148. Hence, molality of the solution is 18.518 mol kg^{-1}. A solution is prepared by dissolving 2.0 g of sucrose and 2.0 g of urea in 100 g of water at 298 K. Calculate the vapour pressure of the solution, if the vapour pressure of pure water at 298 K is 23.56 torr. (Molecular weight of urea = 60 and sucrose = 342)

ISC 2006

Ans :

The expression for Raoult's law for the solution containing non-volatile solute is

$$\frac{\Delta p}{p^\circ} = \frac{p^\circ - p}{p^\circ} = \frac{n}{n+N}$$

$$= \frac{w/m}{w/m + W/M}$$

Here, $p^\circ = 23.56$ torr

Number of moles of solute,

n = Number of moles of sucrose + Number of moles of urea

$$= \frac{w_s}{m_s} + \frac{w_u}{m_u}$$

$$n = \frac{2}{342} + \frac{2}{60}$$

Number of moles of solvent (water),

$$N = \frac{100}{18}$$

$$\frac{23.56 - p}{23.56} = \frac{\frac{2}{342} + \frac{2}{60}}{\frac{2}{342} + \frac{2}{60} + \frac{100}{18}} = 0.007$$

$$23.56 - p = 0.007 \times 23.56 = 0.165$$

$$p = 23.56 - 0.165 = 23.395 \text{ torr}$$

Hence the vapour pressure of the solution is 23.395 torr.

149. Which of the following solutions will have a lower vapour pressure and why?

(i) A 5% solution of cane sugar ($C_{12}H_{22}O_{11}$)

(ii) A 5% solution of urea (NH_2CONH_2).
(Relative atomic masses of H = 1, C = 12, O = 16,N = 14)

ISC 2009

Ans :

Vapour pressure of solution $\propto$ Mole fraction of solvent. Let, 5 g of cane sugar be dissolved in 100 g of water

Mole fraction of water in (i)

$$= \frac{N}{N+n} = \frac{W/M}{\frac{w}{M'} + \frac{W}{M}}$$

$$= \frac{100/18}{100/18 + 5/342}$$

$$= \frac{5.55}{5.55 + 0.0146} = 0.9973$$

$$\left(\text{where, } N = \frac{W}{M} = \frac{100}{18} \text{ and } n = \frac{w}{M'} = \frac{5}{342}\right)$$

Mole fraction of water in (ii),

$$\frac{N}{N+n'} = \frac{\frac{100}{18}}{\frac{100}{18} + \frac{5}{60}} = 0.98526$$

$$\left(\text{where, } n' = \frac{5}{60}\right)$$

Vapour pressure of 5% solution of urea will be lower because mole fraction of water is lower than that of 5% solution of cane sugar.

150. A 0.15 M aqueous solution of KCl exerts an osmotic pressure of 6.8 atm at 310 K. Calculate the degree of dissociation of KCl.
($R = 0.0821$ L atm K^{-1} mol^{-1}).

ISC 2017

Ans :

Osmatic pressure $(\pi) = CRT$

Given, $C = 0.15$ M, $R = 0.0821$ L atm K^{-1}mol^{-1}

$T = 310$ K

$\pi = CRT$

$= 0.15 \text{ M} \times 0.0821 \text{ L atm K}^{-1}\text{mol}^{-1} \times 310 \text{ K}$

$= 3.82$ atm

Observed

$\pi = 6.8$ atm

van't Hoff Factor,

$$i = \frac{\text{Observed magnitude of } \pi}{\text{Normal magnitude of } \pi}$$

$$= \frac{6.8}{3.82} = 1.78$$

If degree of dissociation is α, then for KCl, $n = 2$ as the number of solute particles in its aqueous solution is almost double the number of NaCl molecules.

$$\alpha = \frac{i-1}{n-1} = \frac{1.78 - 1}{2 - 1} = 0.78$$

or $\alpha = 78\%$

151. When 2 g of benzoic acid is dissolved in 25 g of benzene, it shows a depression in freezing point equal to 1.62 K. Molal depression constant (K_f) of benzene is 4.9 K kg mol^{-1} and molecular weight of benzoic acid = 122 g/mol. What will be the percentage association of the benzoic acid?
(Benzoic acid forms dimer when dissolved benzene.)

ISC 2023

NODIA

Ans :

Given, $w_{\text{Benzoic acid}} = 2\,\text{g},\ K_f = 4.9\,\text{K kg mol}^{-1}$

$W_{\text{Benzene}} = 25\,\text{g},\ \Delta T_f = 1.62\,\text{K}$

Now, $$\Delta T_f = K_f \times \frac{w_{\text{Benzoic acid}} \times 1000}{M_{\text{Benzoic acid}} \times W_{\text{Benzene}}}$$

$$1.62 = \frac{4.9 \times 2\,\text{g} \times 1000}{M_{\text{Benzoic}} \times 25\,\text{g}}$$

$$M_{\text{Benzoic acid}} = \frac{4.9 \times 2 \times 1000}{1.62 \times 25} = 241.98\,\text{g/mol}$$

Degree of association of benzoic acid is

$$2C_6H_5COOH \rightleftharpoons (C_6H_5COOH)_2$$

At $t = 0$	1	0
At $t = t_{eq}$	$1 - x$	$x/2$

So, total no. of moles of particles at equilibrium

$$= 1 - x + \frac{x}{2} = 1 - \frac{x}{2} = i$$

$$i = \frac{\text{Normal molecular mass}}{\text{Abnormal molecular mass}}$$

$$1 - \frac{x}{2} = \frac{122}{241.98}$$

$$\frac{x}{2} = 1 - \frac{122}{241.98}$$

$$x = 0.992 = 99.2\%$$

152. When 0.4 g of oxalic acid is dissolved in 40 g of benzene, the freezing point of the solution is lowered by 0.45 K. Calculate the degree of association of acetic acid. Acetic acid forms dimer when dissolved in benzene. (K_f for benzene $= 5.12\,\text{K kg mol}^{-1}$, at. wt. C = 12, H = 1, O = 16))

ISC 2019

Ans :

Given,

Mass of oxalic acid $= 0.4\,\text{g}(w_B)$

Mass of benzene $= 40\,\text{g}\,(W_A)$

K_f for benzene $= 5.12\,\text{K kg mol}^{-1}$

Molar mass of oxalic acid $[C_2O_4H_2] = 90\,\text{g mol}^{-1}$

$(2 \times 12 + 4 \times 16 + 2 \times 1)$, i.e. (M_B)

ΔT_f (lowering in freezing point) $= 0.45\,\text{K}$

Now, $$\Delta T_f = i \times K_f \times \frac{w_B}{M_B} \times \frac{1000}{W_A}$$

$$i = \frac{\Delta T_f \times M_B \times W_A}{K_f \times w_B \times 1000}$$

$$i = \frac{0.45\,\text{K} \times 90\,\text{g mol}^{-1} \times 40\,\text{g}}{5.12\,\text{K kg mol}^{-1} \times 0.4\,\text{g} \times 1000} = 0.79$$

Also, $i = 1 - \alpha + \frac{\alpha}{2}$ (For association)

where, i = van't Hoff factor and

α = degree of association

$$0.79 = 1 - \alpha + \frac{\alpha}{2} = 1 - \alpha\left[1 - \frac{1}{2}\right]$$

$$0.79 = 1 - \frac{\alpha}{2}$$

$$\frac{\alpha}{2} = 1 - 0.79 = 0.21$$

$$\alpha = 0.42 \text{ or } 42\%$$

153. A solution of urea in water has a boiling point of 100.18°C. Calculate the freezing point of the solution.
(K_f for water is $1.86\,\text{K kg mol}^{-1}$ and K_b for water is $0.512\,\text{K kg mol}^{-1}$)

ISC 2012

Ans :

Calculation of molality (m) of the solution

Given, boiling point of solution

$$= 100.18 + 273$$

$$= 373.18\,\text{K}$$

Boiling point of water $= 100 + 273 = 373\,\text{K}$

Elevation in boiling point,

$$\Delta T_b = 373.18^\circ\,\text{K} - 373^\circ\,\text{K} = 0.18\,\text{K}$$

We know that,

$$\Delta T_b = K_b \times m$$

Molality, $$m = \frac{\Delta T_b}{K_b} = \frac{0.18}{0.512} = 0.351\,\text{mol kg}^{-1}$$

(as $K_b = 0.512\,\text{K kg mol}^{-1}$)

Calculation of freezing point

We know that,

$$\Delta T_f = K_f \times m$$

$$= 1.86 \times 0.351 = 0.652\,\text{K}$$

(as $K_f = 1.86\,\text{K kg mol}^{-1}$)

$$T_f = T_f' - \Delta T_f$$

$$= 273\,\text{K} - 0.652\,\text{K} = 272.34\,\text{K}$$

(as freezing point of water $= 0^\circ\,\text{C} = 273\,\text{K}$)

$$T_f = -0.652^\circ\,\text{C}$$

154. An aqueous solution of a non-volatile solute freezes at 272.4 K, while pure water freezes at 273.0 K. Determine the following : (Given, $K_f = 1.86\,\text{K kg mol}^{-1}$, $K_b = 0.512\,\text{K kg mol}^{-1}$ and vapour pressure of water at 298 K = 23.756 mm of Hg)

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(a) The molality of solution.
(b) Boiling point of solution.
(c) The lowering of vapour pressure of water at 298 K.

ISC 2020

Ans :

(a) Given : $T_f = 272.4\,\text{K}$, $T_f^\circ = 273.0\,\text{K}$

$K_f = 1.86\,\text{K kg mol}^{-1}$

$K_b = 0.512\,\text{K kg mol}^{-1}$

Vapour pressure of water at 298 K $= 23.756\,\text{mm Hg}$

$m = ?$

As we know, $\Delta T_f = K_f \times m$

$0.6 = 1.86 \times m$

or $m = \dfrac{0.6}{1.86}$

Thus, molality of solution = 0.323 m

(b) T_b (Boiling point of solution) = ?

We know, $\dfrac{\Delta T_f}{\Delta T_b} = \dfrac{K_f}{K_b}$

$\dfrac{0.6}{\Delta T_b} = \dfrac{1.86}{0.512}$

or $\Delta T_b = \dfrac{0.6 \times 0.512}{1.86} = 0.17\,\text{K}$

Also, $\Delta T_b = T_b - T_b^\circ$

$0.17 = T_b - 273$

$0.17 + 273 = T_b$

$273.17\,\text{K} = T_b$

Boiling point of solution is 273.17 K.

(c) Lowering of vapour pressure at 298 K = ?

We know, $\dfrac{p^\circ - p}{p^\circ} = \dfrac{(760 - 23.756)\,\text{mm Hg}}{760\,\text{mm Hg}}$

$\dfrac{p^\circ - p}{p^\circ} = 0.969$

155. Define osmotic pressure. Arrange the following in increasing order of osmotic pressure and give reasons in support of your answer.

(i) 34.2 g per litre of sucrose (Molecular weight = 342).
(ii) 90.0 g per litre of glucose (Molecular weight = 180).
(iii) 5.85 g per litre of sodium chloride (Molecular weight= 58.5).

ISC 2004

Ans :

The pressure which must be applied to the solution in order to prevent the passage of solvent molecules into the solution through a semipermeable membrane separating the two is called **osmotic pressure**.

Osmotic pressure is a colligative property which depends upon the number of solute particles.

(i) Moles of sucrose $= \dfrac{w_{\text{sucrose}}}{M}$

$= \dfrac{34.2}{342} = 0.1\,\text{mol}$

Since,

1 mole of sucrose $= 6.022 \times 10^{23}$ particles

0.1 mole of sucrose $= 6.022 \times 10^{23} \times 0.1$

$= 6.022 \times 10^{22}$ particles

Hence, 34.2 g per litre of sucrose contains 6.022×10^{22} particles.

(ii) Moles of glucose $= \dfrac{90.0}{180} = 0.5\,\text{mol}$

Since,

1 mole of glucose $= 6.022 \times 10^{23}$ particles

0.5 mole of glucose $= 6.022 \times 10^{23} \times 0.5$

$= 30.11 \times 10^{22}$ particles

$= 3.011 \times 10^{23}$ particles

Hence, 90.0 g per litre of glucose contains 3.011×10^{23} particles.

(iii) Moles of NaCl $= \dfrac{5.85}{58.5} = 0.1\,\text{mol}$

Since, 1 mole of NaCl $= 2 \times 6.023 \times 10^{23}$ particles

$(\text{NaCl} \rightleftharpoons \text{Na}^+ + \text{Cl}^-)$

0.1 mol of NaCl $= 2 \times 6.023 \times 10^{23} \times 0.1$

$= 12.046 \times 10^{22}$ particles

Hence, 5.85 g per litre of NaCl contains 12.046×10^{22} particles.

Among all the above, 90.0 g per litre of glucose contains maximum number of particles followed by NaCl and sucrose.

Thus, glucose would possess maximum osmotic pressure.

The increasing order of their osmotic pressure is sucrose < NaCl < glucose.

C is the molar concentration of solution. On increasing the molar concentration, osmotic pressure increases. If the weight of all solutes and its solution volumes are equal, osmotic pressure will only by depend on molar mass of solute.

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CHAPTER 2

ELECTRO-CHEMISTRY

SUMMARY

1. ELECTROLYTIC CELL

It is a device in which electricity from outside source is used to carry out a reaction (electrolysis). The device or cell used to carry out electrolysis is called electrolytic cell.

2. ELECTROCHEMICAL CELL OR GALVANIC CELL

It is a device in which indirect redox reaction takes place and decrease in energy during the reaction appears in the form of electricity.

3. ELECTROLYSIS OF MOLTEN NACL

In molten state, NaCl consists of Na^+ consist Cl^- ions, On passing electricity, following reactions takes place :

At cathode : $Na^+ + e^- \longrightarrow Na$

At anode : $Cl^- - e^- \longrightarrow Cl$

$Cl + Cl \longrightarrow Cl_2$

The over all reaction :

$$2Na^+(l) + 2Cl^-(l) \longrightarrow 2Na(s) + Cl_2(g)$$

4. ELECTROLYSIS OF ACIDIFIED WATER

It consists of H^+, OH^-, SO_4^{2-} ions.

On passing electricity, following reactions takes place :

At cathode $H^+ + e^- \longrightarrow H$

$H + H \longrightarrow H_2$

At anode $OH^- - e^- \longrightarrow OH$

$4OH \longrightarrow 2H_2O + O_2$

The overall reaction is

$$4H^+(aq) + 4OH^-(aq \longrightarrow 2H_2(g) + 2H_2O(l) + O_2(g)$$

5. ELECTROLYSIS OF CONCENTRATED AQUEOUS NACL

It consists of Na^+, H^+, Cl^- and OH^- ions.

On passing electricity, following reactions takes place :

At cathode : $H^+ + e^- \longrightarrow H$

$H + H \longrightarrow H_2$

At anode : $Cl^- - e^- \longrightarrow Cl$

$Cl + Cl \longrightarrow Cl_2$

The overall reaction is :

$$2H^+(aq) + 2Cl^-(aq) \longrightarrow H_2(g) + Cl_2(g)$$

The solution becomes basic in nature due to the formation of NaOH.

6. ELECTROLYSIS OF AQUEOUS $CuSO_4$

It consists of Cu^{2+}, H^+, SO_4^{2-} and OH^- ions.

On passing electricity, following reaction takes place :

At cathode : $Cu^{2+} + 2e^- \longrightarrow Cu$

At anode : $OH^- - e^- \longrightarrow OH$

$4OH \longrightarrow 2H_2O + O_2$

The overall reaction is :

$$2Cu^{2+}(aq) + 4OH^-(aq) \longrightarrow 2Cu(s) + 2H_2O(l) + O_2(g)$$

The solution becomes acidic in nature due to the formation of H_2SO_4.

7. ELECTROLYSIS OF $CuSO_4$ USING Cu ELECTRODES

It consists of Cu^{2+}, H^+, SO_4^{2-} and OH^- ions.

On passing electricity, following reactions takes place :

At cathode : $Cu^{2+} + 2e^- \longrightarrow Cu$

At anode : $Cu \longrightarrow Cu^{2+} + 2e^-$

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8. FARADAY'S LAW OF ELECTROLYSIS

(a) The amount of substance deposited at any electrode during electrolysis is directly proportional to the quantity of electricity passing i.e.,

$$W \propto Q$$

$$W = zQ$$

or $$W = zIt$$

Where, z = electrochemical equivalent,

W = amount of the substance deposited (g),

I = Strength of current passed (amperes),

t = time (sec).

When $I = 1$ ampere, $t = 1$ sec, then $W = z$.

Thus, electrochemical equivalent of a substance may be defined as the mass of the substance deposited when a current of 1 ampere is passed for one second.

(b) When the same quantity of electricity is passed through solutions of different electrolytes connected in series, then the weights of the substances deposited at the electrodes are directly proportional to their equivalent weights. So,

$$\frac{w_A}{w_B} = \frac{\text{Eq.wt. of } A}{\text{Eq. wt. of } B}$$

9. FARADAY

The charge on one mole of electrons is called 1 Faraday. Thus,

$$1 \text{ Faraday (1F)} = 96500 \text{ C}$$

So, charge on n mole of electrons will be equal to

$$Q = n \text{ F}$$

10. METALLIC CONDUCTORS

Those substance which allow the flow of current by movement of electrons are called metallic conductors.

Example : Cu, Ag, Fe etc.

11. ELECTROLYTIC CONDUCTOR

Those substances which conduct electricity with the chemical decomposition are called electrolytic conductors.

Example : HCl, HNO_3, NaOH etc.

12. CONDUCTANCE (C)

It is the reciprocal of resistance.

$$C = \frac{1}{R}$$

It units are ohm^{-1}(Ω^{-1}) or siemens (S).

13. SPECIFIC RESISTANCE OR RESISTIVITY (ρ)

It is defined as the resistance of a conductor of 1 cm length and having area of cross-section equal to 1 cm^2.

$$\rho = \frac{Ra}{l}$$

Its units are ohm cm or ohm m.

l = Length of conductor in cm

a = Area of cross-section in cm^2

14. CELL CONSTANT

It is defined as the ratio of distance between the electrodes (l) to the area of the electrodes (a).

$$\text{Cell constant} = \frac{l}{a}$$

Its units are cm^{-1}

15. CONDUCTIVITY (κ) OR SPECIFIC CONDUCTANCE

It is reciprocal of resistivity.

$$\kappa \text{ (Kappa)} = \frac{1}{\rho}$$

Its units are ohm^{-1} cm^{-1} or S m^{-1} or Ω^{-1}m^{-1}.

16. EQUIVALENT CONDUCTIVITY ($\wedge_{eq}$)

It is defined as the conductance offered by all the ions formed by dissolving one gram equivalent of the electrolyte in solution.

$$\Lambda_{eq} = \frac{\kappa \times 1000}{\text{Normality}}$$

Its units are ohm^{-1}cm^2 (g equiv)$^{-1}$ or S m^2 eq^{-1}

17. MOLAR CONDUCTIVITY (Λ_m)

It is defined as the conductance offered by all the ions formed by dissolving one mole of an electrolyte in solution.

$$\Lambda_m = \frac{\kappa \times 1000}{\text{Molarity}}$$

Its units are ohm^{-1} cm^2 mol^{-1} or S m^2 mol^{-1}

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18. KOHLRAUSCH'S LAW

According to this law, "the molar conductivity of a weak electrolyte at infinite dilution is the sum of the ionic conductivities of all the ions at infinite dilution each multiplied with the number of ions present in the formula unit of the electrolyte." So,

$$\Lambda_m^\infty(A_xB_y) = x\Lambda_m^\infty(A^{y+}) + y\Lambda_m^\infty(B^{x-})$$

19. APPLICATION OF KOHLRAUSCH'S LAW

The application of Kohlrausch's law are as follows:

1. In the calculation of Λ_m^∞ for weak electrolyte
2. In the calculation of degree of dissociation

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^\infty}$$

3. In the calculation of dissociation constant of weak electrolyte.

$$\kappa = \frac{C\alpha^2}{1-\alpha}$$

4. In the calculation of solubility of weak electrolyte.

$$\text{Solubility} = \frac{k'1000}{\Lambda_{eq}^\infty}$$

20. REPRESENTATION OF ELECTROCHEMICAL CELL

The following conventions are used to represent the electrochemical cell. The Daniel cell is represented as follow:

$$\underset{\text{Anode (Oxidation)}}{\text{Zn(s)}} \mid \text{Zn}^{2+}(\text{C}_1\text{M}) \parallel \underset{\text{Salt bridge}}{\text{Cu}^{2+}}(\text{C}_2\text{M}) \mid \underset{\text{Cathode (Reduction)}}{\text{Cu(s)}}$$

21. STANDARD HYDROGEN ELECTRODE

It is reference electrode and used to measure the electrode potential of any metal electrode. It can act both as anode and cathode. Its electrode potential is assumed to be zero.

22. ELECTROCHEMICAL SERIES

The arrangement of different metal electrodes in the increasing order of standard reduction potentials is called electrochemical series.

23. APPLICATIONS OF ELECTROCHEMICAL SERIES

1. **To compare the oxidising and reducing powers of electrodes:**

$$\text{Oxidising power} \propto \text{Reduction potential}$$

$$\text{Reducing power} \propto \frac{1}{\text{Reduction potential}}$$

2. **To compare the reactivity of a metal :**

$$\text{Reaction of a metal} \propto \frac{1}{\text{Reduction potential}}$$

3. **To calculate the standard of E.M.F. of a cell :**

$$\text{E.M.F. of a cell } (E_{\text{cell}}^\circ) = E_{\text{oxidn}}^\circ + E_{\text{redn}}^\circ$$
$$= E_{\text{cathode}}^\circ + E_{\text{anode}}^\circ$$

4. **To predict the spontaneity of a reaction :**
If the E.M.F. of the cell is positive, then the cell reaction is spontaneous or possible.

24. NERNST EQUATION

This equation gives a relation between electrode potential and concentration of metal ions.

For a general electrode reaction

$$\text{M}^{n+}(\text{aq}) + \text{ne}^- \longrightarrow \text{M(s)}$$

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{2.303\,RT}{n\,\text{F}}\log\frac{1}{[\text{M}^{n+}(\text{aq})]}$$

$$E_{\text{cell}} = \text{E}_{\text{cell}}^\circ - \frac{0.0591}{n}\log\frac{1}{[\text{M}^{n+}(\text{aq})]} \text{ at 298 K}$$

$$E_{\text{cell}} = E_{\text{cell}}^\circ + \frac{0.0591}{n}\log[\text{M}^{n+}(aq)] \text{ at 298 K}$$

25. APPLICATIONS OF NERNST EQUATION

The applications of Nernst equation are as follows:

1. **Calculate of E.M.F. of a cell :**
For the cell reaction :

$$aA + bB \underset{}{\overset{ne^-}{\rightleftharpoons}} cC + dD$$

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{2.303\,\text{RT}}{n\,\text{F}}\log\frac{[\text{Oxidised state}]}{[\text{Reduced state}]}$$

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0591}{n}\log\frac{[\text{Oxidised state}]}{[\text{Reduced state}]} \text{ at 298 K}$$

$$E_{\text{cell}} = E_{\text{cell}}^\circ + \frac{0.0591}{n}\log\frac{[\text{Reduced state}]}{[\text{Oxidised state}]} \text{ at 298 K}$$

2. Calculation of conc. of a solution of half-cell by measuring E.M.F. of the cell using Nernst equation.
3. Calculation of equilibrium constant K_c

$$E_{\text{cell}}^\circ = \frac{2.303\,RT}{n\,\text{F}}\log K_c$$

or

$$E_{\text{cell}}^\circ = \frac{0.0591}{n}\log K_c$$

(at equilibrium, $E_{\text{cell}}^\circ = 0$)

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26. COMMERCIAL CELLS

There are two types of commercial cells are as follows :

1. **Primary cells :** In these cells, the electrode reactions cannot be reversed by external electric source.
   Example : Dry cell, mercury cell.
2. **Secondary cells :** In these cells, the electrode reactions can be reversed by an external source.
   Examples : Lead storage battery, nickel cadmium storage cell.

27. DRY CELL

This cell is based upon leclanche cell. In this cell

Zinc cylinder - acts an anode

Graphite rod - acts as cathode

$NH_4Cl + ZnCl_2$ - acts as electrolyte

When the cell is working, the following reactions take place :

At anode : $Zn(s) \longrightarrow Zn^{2+} + 2e^-$

At cathode :

$2MnO_2(s) + 2NH_4 + (aq) + 2e^-$

$\longrightarrow Zn^{2+}(aq) + Mn_2O_3(s) + 2NH_3(g) + H_2O(l)$

The overall cell reaction is :

$Zn(s) + 2NH_4^+(aq) + 2MnO_2(s)$

$\longrightarrow Zn^{2+}(aq) + Mn_2O_3(s) + 2NH_3(g) + H_2O(l)$

The NH_3 gas produced reacts with $ZnCl_2$ to form of complex for avoiding bursting.

$$2NH_2 + ZnCl_2 \longrightarrow [Zn(NH_3)_2Cl_2]$$

This cell does not work for a long time because acidic NH_4Cl corrodes the zinc vessel.

28. MERCURY CELL

In this cell :

Zinc vessel - acts as anode

Mercury (II) oxide - acts as cathode

$KOH + ZnO$ - acts as electrolyte

When the cell is working, the following reactions take place :

At anode :

$Zn(s) + 2OH^-(aq) \longrightarrow ZnO(s) + H_2O(l) + 2e^-$

At anode :

$HgO(s) + H_2O(l) + 2e^- \longrightarrow Hg(l) + 2OH^-$

The overall cell reaction is :

$Zn(s) + HgO(s) \longrightarrow ZnO(s) + Hg(l)$

In this case, the overall cell reaction does not involve any ion in solution whose conc. can change due to which this cell can work for a long time.

29. LEAD STORAGE BATTERY OR CELL

In this battery or cell :

Pb plates – act as anode

PbO_2 plates – acts as cathode

Conce. H_2SO_4 (38%) – acts as electrode

When the batter works, the following reaction take place : (During discharging)

At anode : $Pb(s) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s) + 2e^-$

At cathode :

$PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow 2PbSO_4(s) + 2H_2O(l)$

The overall cell reaction is :

$Pb(s) + PbO_2(s) + 4H^+(aq) + 2SO_4^{2-}(aq) \longrightarrow 2PbSO_4(s) + 2H_2O(l)$

So, H_2SO_4 is used up during its working. At this time battery needs recharging.

During recharging : Electrical energy is supplied to the batter from an external source. The following reaction takes place during this process and the battery becomes ready to work again :

$2PbSO_4(s) + 2H_2O(l) \longrightarrow Pb(s) + PbO_2(s) + 4H^+(aq) + 2SO_4^{2-}(aq)$

30. NI-CD STORAGE CELL

In this cell :

Cd rods – acts as anode

NiO_2 rods – acts as cathode

Dil. KOH – acts as electrolyte

When the cell works, the following reactions take place :

At anode :

$Cd(s) + 2OH^-(aq) \longrightarrow Cd(OH)_2(s) + 2e^-$

At cathode :

$NiO_2(s) + 2H_2O(l) + 2e^- \longrightarrow Ni(OH)_2(s) + 2OH^-(aq)$

The overall cell reaction is :

$Cd(s) + NiO_2(s) + 2H_2O(l) \longrightarrow Cd(OH)_2(s) + Ni(OH)_2(s)$

So, KOH is used up during its working. At this time cell needs recharging.

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During recharging : Electrical energy is supplied to the cell from an external source. The following reaction takes place during this process and the cell becomes ready to work again :

$$Cd(OH)_2(s) + Ni(OH)_2 \longrightarrow Cd(s) + NiO_2(s) + 2H_2O(l)$$

31. $H_2 - O_2$ FUEL CELL

In fuel cell, the energy produced during the combustion of fuels is directly converted into electrical energy.

In this cell, H_2 and O_2 gases are bubbled through a porous carbon electrode into conc. aqueous KOH or NaOH. Each electrode is coated with catalyst (Pt, Ag etc.). During the working of the cell, the following reactions take place :

At anode :

$$2H_2(g) + 4OH^-(aq) \longrightarrow 4H_2O(l) + 4e^-$$

At cathode :

$$O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$$

The overall cell reaction is :

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$$

Advantages of fuel cell :

1. It is pollution free.
2. Its efficiency is high.
3. It is light in weight.
4. It can work for a long time by the continuous supply of H_2 and O_2.

Disadvantages of fuel cell :

1. High cost of catalyst used.
2. Problem to hold gaseous fuel at low temperature or high pressure.

32. CORROSION

The process of slow conversion of a metal into unwanted materials by the reaction with moisture and oxygen present in atmosphere is called corrosion. **Example :** Rusting of iron.

33. ELECTROCHEMICAL THEORY OF RUSTING OF IRON

Impure iron surface acts as electrochemical cell in the presence of water called corrosion cell.

In these cell :

Pure iron – acts as anode

impure iron – acts as cathode ($Fe_2O_3.xH_2O$)

Water + moisture – act as electrolyte

The following reactions take place at the surface of iron :

At anode : $Fe \longrightarrow Fe^{2+} + 2e^-$

At cathode : $2H^+ + \frac{1}{2}O_2 + 2e^- \longrightarrow H_2O$

The net reaction is :

$$Fe + 2H^+ + \frac{1}{2}O_2 \longrightarrow Fe^{2+} + H_2O$$

At iron surface :

$$2Fe^{2+} + \frac{1}{2}O_2 + 2H_2O \longrightarrow Fe_2O_3 + 4H^+$$

$$Fe_2O_3 + xH_2O \longrightarrow \underset{\text{(Rust)}}{Fe_2O_3.x\,H_2O}$$

34. PREVENTION OF CORROSION

The rusting of iron can be prevented by the following method :

1. Barrier protection
2. Sacrificial protection
3. Cathodic protection
4. Using anti-rust solution

OBJECTIVE QUESTIONS

1. The unit of equivalent conductance is

ISC 2010

(a) $ohm^{-1}cm^2\,equiv^{-1}$ (b) $ohm^{-1}\,cm^2\,g^{-1}$

(c) $ohm\,cm^2\,equiv^{-1}$ (d) $ohm^{-1}\,mol^{-1}$

Ans : (a) $ohm^{-1}cm^2\,equiv^{-1}$

Equivalent conductance is the conductance of ions produced by one gram equivalent of an electrolyte dissolved in a solution. Therefore, its unit is written as $ohm^{-1}\ cm^2\ equiv^{-1}$.

2. Electrochemical equivalent is the amount of substance which gets deposited from its solution on passing electrical charge equal to

ISC 2021-22 (Sem-I), 2016

(a) 96500 C (b) 1 C

(c) 60 C (d) 965 C

Ans : (a) 96500 C

Electrochemical equivalent (ECE) is defined as the mass of a substance deposited or liberated during electrolysis when 1 coulomb of electric charge passes through the solution. Its SI unit is kilogram per coulomb (kg/C).

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3. The number of Faraday's required to reduce one mole of Cu^{2+} to metallic copper is

ISC 2009

(a) one (b) two

(c) three (d) four

Ans : (b) two

Number of electrons give the number of Faraday's required for the number of moles of that substance in the balanced equation.

$$Cu^{2+} + 2e^- \longrightarrow Cu$$

The reduce 1 mole of $Cu^{2+} \longrightarrow Cu$, we need 2 moles of e^-. Hence, 2 F required. Thus, the option (b) is correct.

4. Which one of the following statements is true for the Galvanic cell?

ISC 2023

(a) Electrons flow from copper electrode to zinc electrode.

(b) Current flows from zinc electrode to copper electrode.

(c) Cations move towards copper electrode.

(d) Cations move towards zinc electrode.

Ans : (c) Cations move towards copper electrode.

In Galvanic cell, cations move towards Cu electrode (cathode) and accumulated as Cu metal.

5. For a spontaneous reaction E°_{cell} and ΔG° will be respectively

ISC Specimen 2023, Specimen 2021-22 (Sem-I), 2017

(a) negative and negative

(b) negative and positive

(c) positive and negative

(d) positive and positive

Ans : (c) positive and negative

For a spontaneous reaction, E°_{cell} and ΔG° will be positive and negative respectively.

6. The standard electrode potentials of four elements A, B, C and D are -3.05, 1.66, -0.40 and 0.80 V, respectively. The highest chemical activity will be shown by

ISC 2006

(a) A (b) B

(c) C (d) D

Ans : (a) A

Element with large negative electrode potential acts as strong reducing agent and thus, possesses large chemical reactivity.

Hence, (A) shows highest chemical activity among the given options.

7. On dilution, the specific conductance of a solution

ISC Specimen 2021-22 (Sem-1)

(a) remains unchanged

(b) increases

(c) decreases

(d) first increases then decreases

Ans : (c) decreases

Specific conductance depends on the number of ions present per unit volume of the solution. On dilution, the concentration of ions decreases because the volume increases. Although ions move more freely, the number of ions per unit volume becomes less, so the specific conductance decreases.

8. A student noticed that molar conductivity of acetic acid increases sharply on dilution. This is because:

ISC 2020

(a) Number of ions per unit volume increases

(b) Degree of ionisation of acetic acid increases

(c) Resistance of solution becomes zero

(d) Conductivity of water decreases

Ans : (b) Degree of ionisation of acetic acid increases

Acetic acid is a weak electrolyte and ionises only partially in concentrated solution. On dilution, ionisation increases significantly, producing more ions. Greater ionic concentration increases molar conductivity sharply, unlike strong electrolytes where increase is comparatively smaller.

9. In electrolysis of acidified water, oxygen gas is obtained at anode because:

ISC 2010

(a) Hydrogen ions undergo oxidation

(b) Water molecules gain electrons

(c) Water molecules lose electrons at anode

(d) Sulphuric acid decomposes completely

Ans : (c) Water molecules lose electrons at anode

During electrolysis of acidified water, oxidation occurs at anode. Water molecules lose electrons and form oxygen gas along with hydrogen ions. Sulphuric acid only increases conductivity and does not itself undergo decomposition during the overall process.

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10. A lead storage battery is considered a secondary cell because:

ISC 2024

(a) It generates electricity without chemical reaction

(b) Its reactions can be reversed during recharging

(c) It works only once and becomes useless

(d) Its electrolyte remains unchanged permanently

Ans : (b) Its reactions can be reversed during recharging

In lead storage batteries, discharge reactions convert Pb and PbO_2 into $PbSO_4$. During recharging, external electrical energy reverses these reactions and restores original reactants. Hence the battery can be reused repeatedly and is classified as a secondary cell.

11. A metal having more negative reduction potential is generally:

ISC 2021, 2017

(a) Stronger oxidising agent

(b) Less reactive metal

(c) Stronger reducing agent

(d) More noble in nature

Ans : (c) Stronger reducing agent

Metals with highly negative reduction potentials lose electrons more readily and undergo oxidation easily. Therefore they behave as strong reducing agents and show greater chemical reactivity compared to metals with positive reduction potentials.

12. A student connected zinc and copper electrodes to form a Daniell cell. Electrons will flow from zinc to copper because:

ISC 2022

(a) Copper undergoes oxidation more easily

(b) Zinc has greater tendency to lose electrons

(c) Copper ions are stronger reducing agents

(d) Salt bridge pushes electrons towards copper

Ans : (b) Zinc has greater tendency to lose electrons

Zinc possesses lower reduction potential and greater tendency to undergo oxidation. Therefore zinc loses electrons and acts as anode. Electrons released travel through external circuit towards copper electrode where reduction takes place.

13. During corrosion of iron, rust formation occurs mainly due to:

ISC 2016, 2010

(a) Reduction of iron atoms

(b) Oxidation of iron in presence of moisture and oxygen

(c) Direct combination of iron with nitrogen

(d) Deposition of metallic impurities on iron surface

Ans : (b) Oxidation of iron in presence of moisture and oxygen

Rusting is an electrochemical process involving oxidation of iron in presence of moisture and oxygen. Iron loses electrons to form Fe^{2+} ions, which further react to produce hydrated ferric oxide known as rust.

14. In a hydrogen–oxygen fuel cell, electrical energy is produced because:

ISC 2018

(a) Combustion heat directly rotates turbine

(b) Hydrogen and oxygen react electrochemically

(c) Water decomposes spontaneously

(d) Potassium hydroxide acts as fuel

Ans : (b) Hydrogen and oxygen react electrochemically

In a fuel cell, hydrogen undergoes oxidation and oxygen undergoes reduction at separate electrodes. The redox reaction occurs electrochemically and directly converts chemical energy into electrical energy with water as the only product.

15. A student observed that pure water conducts electricity very poorly, whereas acidified water conducts readily. This is because:

ISC 2024

(a) Pure water contains large number of free electrons

(b) Acidified water contains more mobile ions

(c) Sulphuric acid increases temperature of water

(d) Water molecules become metallic after acidification

Ans : (b) Acidified water contains more mobile ions

Pure water ionises only slightly and therefore contains very few ions. Addition of sulphuric acid increases concentration of mobile ions such as H^+ and SO_4^{2-}, thereby increasing electrical conductivity and facilitating electrolysis.

NODIA

16. A galvanic cell with positive EMF indicates that the cell reaction is:

ISC 2018

(a) Non-spontaneous

(b) At equilibrium

(c) Spontaneous

(d) Impossible under standard conditions

Ans : (c) Spontaneous

Positive EMF indicates that free energy change for the reaction is negative. Therefore the redox reaction proceeds spontaneously and chemical energy is converted into electrical energy within the electrochemical cell.

17. A student measured conductivity of an electrolyte solution and found that conductivity decreased on dilution. The decrease occurs because:

ISC 2011

(a) Ionisation completely stops on dilution

(b) Number of ions per unit volume decreases

(c) Resistance of electrodes increases

(d) Current converts into heat energy

Ans : (b) Number of ions per unit volume decreases

Although dilution may increase ionisation, the number of ions present per unit volume decreases significantly. Therefore conductivity decreases because fewer ions are available to carry current through a given volume of solution.

18. During electrolysis of molten NaCl, sodium metal is obtained instead of hydrogen gas because:

ISC 2020, 2016

(a) Water is absent in molten state

(b) Sodium ions possess highest oxidation potential

(c) Chloride ions block hydrogen discharge

(d) Cathode becomes positively charged

Ans : (a) Water is absent in molten state

In molten NaCl, only Na^+ and Cl^- ions are present because water is absent. Therefore Na^+ ions are reduced at cathode to form sodium metal instead of hydrogen gas.

19. A dry cell does not function effectively for long periods because:

ISC 2012

(a) Graphite rod melts continuously

(b) NH_4Cl corrodes the zinc container

(c) MnO_2 acts as reducing agent permanently

(d) Zinc ions block electron movement

Ans : (b) NH_4Cl corrodes the zinc container

The acidic NH_4Cl paste used as electrolyte gradually corrodes the zinc container acting as anode. This damages the cell and reduces its efficiency after prolonged use.

20. A metal placed higher in the electrochemical series generally:

ISC 2017

(a) Has greater tendency to gain electrons

(b) Acts as stronger oxidising agent

(c) Has greater tendency to lose electrons

(d) Shows lower chemical reactivity

Ans : (c) Has greater tendency to lose electrons

Metals placed higher in electrochemical series possess more negative reduction potentials and therefore lose electrons more easily. Hence they are stronger reducing agents and more reactive metals.

21. The salt bridge in a galvanic cell is mainly used to:

ISC 2021

(a) Increase electrode potential

(b) Maintain electrical neutrality of solutions

(c) Produce electrons continuously

(d) Prevent oxidation at anode

Ans : (b) Maintain electrical neutrality of solutions

During cell operation, excess positive and negative charges develop in half-cells. Salt bridge allows migration of ions and maintains electrical neutrality, thereby enabling continuous flow of electrons through the external circuit.

22. A student electroplated an iron spoon with silver using electrolysis. The spoon was connected to:

ISC 2025

(a) Anode because reduction occurs there

(b) Cathode because metal deposition occurs there

(c) Salt bridge to increase conductivity

(d) Positive terminal to attract silver atoms

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Ans : (b) Cathode because metal deposition occurs there

During electroplating, the object to be coated is connected as cathode. Metal ions gain electrons at cathode and get deposited as a thin metallic layer over the surface.

23. Rusting of iron occurs more rapidly in coastal regions because:

ISC 2021

(a) Moist air increases electrochemical corrosion

(b) Oxygen is absent near sea water

(c) Salt water decreases conductivity completely

(d) Iron becomes chemically inert near sea water

Ans : (a) Moist air increases electrochemical corrosion

Moisture and dissolved salts present in coastal air increase conductivity of water layer on iron surface. This accelerates electrochemical corrosion and therefore rusting becomes faster in coastal regions.

24. A hydrogen electrode is considered a reference electrode because:

ISC 2004

(a) Its electrode potential is fixed as zero

(b) It produces maximum current in all cells

(c) Hydrogen never undergoes oxidation

(d) Platinum acts as electrolyte

Ans : (a) Its electrode potential is fixed as zero

Standard hydrogen electrode is assigned zero electrode potential by convention. Therefore it is used as reference electrode for measuring standard electrode potentials of other half-cells.

25. A student observed bubbles of chlorine gas near one electrode during electrolysis of concentrated aqueous NaCl. The electrode where chlorine is liberated is:

ISC 2025

(a) Cathode because reduction occurs there

(b) Anode because oxidation of chloride ions occurs there

(c) Cathode because sodium ions are discharged first

(d) Salt bridge because ions accumulate there

Ans : (b) Anode because oxidation of chloride ions occurs there

During electrolysis of concentrated NaCl solution, chloride ions lose electrons at the anode to form chlorine gas. Oxidation always occurs at the anode. Sodium ions are not discharged because reduction of water is energetically more favourable in aqueous medium.

NODIA

26. When zinc granule is dipped into copper sulphate solution, copper is precipitated because

ISC Specimen 2021-22 (Sem-I), 2011

(a) both copper and zinc have a positive reduction potential.

(b) both copper and zinc have a negative reduction potential.

(c) reduction potential of zinc is higher than that of copper.

(d) reduction potential of copper is higher than that of zinc.

Ans : (d) reduction potential of copper is higher than that of zinc.

$$Zn + CuSO_4 \longrightarrow ZnSO_4 + \underset{\text{ppt.}}{Cu} \downarrow$$

Zn reducing the Cu due to its high reduction potential than Cu.

27. The number of Faraday's which will be required to reduce 4 g equivalents of Cu^{2+} to Cu metal is

ISC 2005

(a) 1 (b) 2

(c) 3 (d) 4

Ans : (d) 4

Given, $\underset{\text{4 g equivalents}}{Cu^{2+}} + 2e^- \longrightarrow Cu$

According to Faraday's first law of electrolysis, 1 F is the electrical charge required to deposit one gram equivalent of substance.

$$\underset{\substack{\text{1 mol}\\ \text{4 g equivalents}}}{Cu^{2+}} + \underset{\substack{\text{2 mol of } e^-\\ \text{4 g equivalents}}}{2\ e^-} \longrightarrow \underset{\substack{\text{1 mol}\\ \text{4 g equivalents}}}{Cu}$$

(According to mole concept)
(According to law of equivalent)

Therefore, the number of Faraday's required to reduce 4 g equivalents of Cu^{2+} to Cu metal is 4.

28. A galvanic cell stopped producing current after prolonged use because:

ISC 2021

(a) Oxidation and reduction reactions reached equilibrium

(b) Salt bridge started producing electrons

(c) Electrode potential became infinite

(d) Electrolyte stopped ionising completely

Ans : (a) Oxidation and reduction reactions reached equilibrium

In a galvanic cell, current is produced due to spontaneous redox reaction. After long use, reactants become depleted and equilibrium is established. At equilibrium, cell EMF becomes zero and electron flow stops, causing the cell to stop functioning.

29. A concentrated solution of $CuSO_4$ was electrolysed using copper electrodes. The concentration of $CuSO_4$ remained nearly unchanged because:

ISC 2022

(a) Copper deposited at cathode equals copper dissolved at anode

(b) Sulphate ions completely disappear during electrolysis

(c) Water undergoes oxidation instead of copper

(d) Copper ions are not involved in electrode reactions

Ans : (a) Copper deposited at cathode equals copper dissolved at anode

Copper ions are reduced at cathode forming copper metal, while equal amount of copper dissolves from anode producing Cu^{2+} ions. Therefore concentration of $CuSO_4$ solution remains nearly constant during electrolysis using copper electrodes.

30. The ionic conductance at infinite dilution for Ba^{2+} and Cl^- ions are 127 $ohm^{-1}cm^2mol^{-1}$ and 76 $ohm^{-1}cm^2mol^{-1}$ respectively. What will be the molar conductance of $BaCl_2$ at infinite dilution?

ISC 2021-22 (Sem-1)

(a) 139.5 $ohm^{-1}cm^2mol^{-1}$

(b) 279.0 $ohm^{-1}cm^2mol^{-1}$

(c) 203.0 $ohm^{-1}cm^2mol^{-1}$

(d) 101.5 $ohm^{-1}cm^2mol^{-1}$

Ans : (b) 279.0 $ohm^{-1}cm^2mol^{-1}$

The equivalent weight of

$$BaCl_2 = \frac{\text{molecular weight}}{2}$$

$$\lambda^\circ_m \text{ for } BaCl_2 = \lambda^\circ_{m(Ba^{2+})} + 2\lambda^\circ_{m(Cl^-)}$$

$$= 127 + 76 \times 2$$

$$= 279\ ohm^{-1}cm^2mol^{-1}$$

31. The standard reduction electrode potential of Cu^{2+}/Cu is $+0.34$ V and that of Cr^{3+}/Cr is -0.74 V.These two electrodes are connected in their standard state to make an electrochemical cell. What will be the standard electrode potential (E°) of this cell ?

ISC 2021-22 (Sem-I)

(a) 1.19 V (b) 1.08 V

(c) 0.69 V (d) 1.83 V

Ans : (b) 1.08 V

At cathode,

$$Cu^{2+} + 2e^- \longrightarrow Cu,\ E^\circ_{cell} = 0.34\ V$$

At anode, $$Cr \longrightarrow Cr^{3+} + 3e^-,$$

$$E^\circ_{cell} = -0.74\ V$$

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

$$= 0.34 - (-0.74) = 1.08\ V$$

32. The quantity of electricity required to deposit 1.15 g of sodium from molten NaCl (Na = 23, Cl = 35.5) is

ISC 2012

(a) 1 F (b) 0.5 F

(c) 0.05 F (d) 1.5 F

Ans : (c) 0.05 F

Given, weight of Na = 1.15 g

In molten state, NaCl ionises is

$$\underset{\text{Molten}}{NaCl} \longrightarrow Na^+ + Cl^-$$

and $$Na^+ + e^- \longrightarrow Na$$

1 Faraday will deposit 1 mole of Na, i.e. 23 g.

The quantity of electricity required to deposit 23 g of Na from NaCl = 1 F

1.15 g of Na will be deposited by

$$\frac{1 \times 1.15}{23}\ F = 0.05\ F$$

33. The standard reduction potential values of three metallic cations X, Y and Z are 0.52 V, – 3.03 V and – 1.18 V respectively. The order of reducing power of the corresponding metals is

ISC Specimen 2021-22 (Sem-I)

(a) $Y > Z > X$ (b) $X > Y > Z$

(c) $Z > Y > X$ (d) $Z > X > Y$

Ans : (a) $Y > Z > X$

The reducing power of a metal depends upon its tendency to lose electrons. A metal having a more negative standard reduction potential (E) loses electrons more easily and therefore acts as

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a stronger reducing agent. The given standard reduction potential values are: X=+0.52V, Y=-3.03V and Z=-1.18V. Since Y has the most negative reduction potential, it has the greatest tendency to lose electrons and hence is the strongest reducing agent. Next comes Z, while X, having a positive reduction potential, is the weakest reducing agent. Therefore, the order of reducing power of the metals is:

$$Y > Z > X$$

34. The cell reaction is spontaneous or feasible when emf of the cell is

ISC 2019

(a) negative

(b) positive

(c) zero

(d) either positive or negative

Ans : (b) positive

Free energy, i.e. ΔG° must be negative for a cell reaction to be spontaneous or feasible and

$$\Delta G^\circ = -nFE^\circ_{cell} = (-)\text{ve}$$

where, n = number of electrons

F = charge in Faraday

E° = emf of the cell

Therefore, E°_{cell}, i.e. emf of the cell must be positive.

35. The limiting molar conductivities (Λ^∞_m) for NaCl, KBr and KCl are 126, 152 and 150 $\text{ohm}^{-1}\,\text{cm}^2\,\text{mol}^{-1}$ respectively.

ISC Specimen 2021-22 (Sem-I)

(i) The molar conductivity at infinite dilution for NaBr is

(a) $128\,\text{ohm}^{-1}\,\text{cm}^2\,\text{mol}^{-1}$

(b) $176\,\text{ohm}^{-1}\,\text{cm}^2\,\text{mol}^{-1}$

(c) $278\,\text{ohm}^{-1}\,\text{cm}^2\,\text{mol}^{-1}$

(d) $302\,\text{ohm}^{-1}\,\text{cm}^2\,\text{mol}^{-1}$

Ans : (a) $128\,\text{ohm}^{-1}\,\text{cm}^2\,\text{mol}^{-1}$

$$\Lambda_{NaBr} = \Lambda^\circ_{NaCl} + \Lambda^\circ_{KBr} - \Lambda^\circ_{KCl}$$

$$\Lambda_{NaBr} = (1.26 + 152 - 150)\,\text{S cm}^2\text{mol}^{-1}$$

$$= 128\,\text{S cm}^2\text{mol}^{-1}$$

(ii) The law applied to determine the molar conductivity of infinite dilution is known as

(a) Faraday's law (b) Avogadro's law

(c) Kohlrausch law (d) Ohm's law

Ans : (c) Kohlrausch law

Kohlrausch law is used to find the molar conductivity of weak electrolyte using strong electrolytes at infinite dilution.

36. The standard reduction electrode potential for Sn^{4+}/Sn^{2+} couple is $+0.15\,\text{V}$ and that for the Cr^{3+}/Cr couple is $-0.74\,\text{V}$. These two couples in their standard state are connected to make a cell (1 Faraday = 96500 C mol^{-1}).

ISC 2021-22 (Sem-I)

At cathode, $(Sn^{4+} + 2e^- \longrightarrow Sn^{2+}) \times 3$

At anode, $(Cr \longrightarrow Cr^{3+} + 3e^-) \times 2$

Hence, $n = 6$

(i) What will be the value of E°_{cell}?

(a) +1.19 V (b) + 0.89 V

(c) + 0.18 V (d) +1.83 V

Ans : (b) + 0.89 V

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

$$= 0.15 - (-0.74) = 0.89\,\text{V}$$

(ii) What will be the value of standard Gibbs energy (ΔG°) ?

(a) – 650.3 kJ (b) – 515.3 kJ

(c) – 226.4 kJ (d) – 406.8 kJ

Ans : (b) – 515.3 kJ

$$\Delta G^\circ = -nFE^\circ_{cell}$$

$$= -6 \times 96500 \times 0.89 = -515.3\,\text{kJ}$$

37. The standard electrode potential for the reaction is

ISC Specimen 2021-22 (Sem-I)

I. $Ag^+ + e^- \longrightarrow Ag(s)$; $E^\circ_{Ag^+/Ag} = +0.80\,\text{V}$

II. $Sn^{2+} + 2e^- \longrightarrow Sn(s)$; $E^\circ_{Sn^{2+}/Sn} = -0.14\,\text{V}$

(i) The E°_{cell} will be

(a) 0.66 V (b) 0.88 V

(c) 0.94 V (d) 1.08 V

Ans : (c) 0.94 V

At anode, $Sn \longrightarrow Sn^{2+} + 2e^-$

At cathode, $\dfrac{[Ag^+ + e^- \longrightarrow Ag] \times 2}{Sn + 2Ag^+ \longrightarrow Sn^{2+} + 2Ag}$

So, $n = 2$

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

$$= -0.80 - (-0.14)$$

$$E^\circ_{cell} = 0.94\,\text{V}$$

NODIA

(ii) The value of standard Gibbs energy (ΔG°) will be ($F = 96{,}000$ C mol^{-1})

(a) – 181.42 kJ (b) – 90.71 kJ

(c) – 45.36 kJ (d) – 22.68 kJ

Ans : (a) – 181.42 kJ

$$\Delta G^\circ = -nFE^\circ_{cell}$$
$$= -2 \times 96500 \times 0.94$$
$$= 181420 \text{ J} = -181.42 \text{ kJ}$$

38. A current liberates 0.50 g of hydrogen in 2 h. The weight of copper (atomic weight = 63.5) deposited at the same time by the same current through copper sulphate solution is

ISC 2014

(a) 63.5 g (b) 31.8 g

(c) 15.9 g (d) 15.5 g

Ans : (b) 31.8 g

Given, weight of hydrogen deposited in

$$2 \text{ h} = 0.50 \text{ g}$$

Atomic weight of Cu = 63.5 g

From Faraday's second law, 'the amount of substance obtained by the same quantity of electricity is directly proportional to their equivalent weights'.

Hence,

$$\frac{\text{Weight of hydrogen}}{\text{Weight of copper}} = \frac{\text{Equivalent weight of hydrogen}}{\text{Equivalent weight of copper}}$$

Let, w is the weight of Cu,

Then $$\frac{0.5}{w} = \frac{1}{63.5}$$

Equivalent weight of H = 1

Equivalent weight of Cu = 63.5

$$w = 63.5 \times 0.5$$
$$= 31.75 \approx 31.8 \text{ g}$$

39. When two Faradays of electricity is passed through an aqueous solution of $CuSO_4$ and an aqueous solution of $AgNO_3$.

(Atomic weight of Cu = 63.5 g mol^{-1}, Ag = 108 g mol^{-1})

ISC 2019

(i) The mass of copper deposited at the cathode is

(a) 127.02 g (b) 63.50 g

(c) 31.75 g (d) 15.87 g

Ans : (b) 63.50 g

The reaction is $Cu^{2+} + 2e^- \longrightarrow Cu$

2 moles of electrons react with 1 mole of Cu^{2+} to deposit 1 mole of Cu = 63.5 g of copper.

We know,

2 Faradays of electricity corresponds to 2 moles of electrons. Hence, they will deposit 63.5 g of Cu at cathode.

(ii) The mass of silver deposited at the cathode is

(a) 54 g (b) 108 g

(c) 216 g (d) 270 g

Ans : (c) 216 g

Reaction at cathode is $Ag^+ + e^- \longrightarrow Ag$

1 mole of electron react with 1 mole of Ag^+ to deposit 1 mole of Ag = 108 g mol^{-1}

2 Faradays of electricity corresponds to 2 moles of electrons.

So, 2 Faradays of electricity

$$= 2 \times 1 \text{ mole of } Ag^+$$
$$= 2 \times 1 \text{ mole of Ag deposited at cathode}$$
$$= 2 \times 108 \text{ g mol}^{-1}$$
$$= 216 \text{ g mol}^{-1}$$

40. A solution containing 2 g of anhydrous barium chloride in 400 cm^3 of water has a specific conductivity of 0.0058 S cm^{-1}. (At. wt. of Ba = 137, Cl = 35.5)

(i) What is the molarity of the above solution?

(a) 0.204 M (b) 0.024 M

(c) 0.420 M (d) 4.021 M

Ans : (b) 0.024 M

Step I. Analysing the given data

Mass of $BaCl_2$ = 2 g

Molar mass of $BaCl_2$ = 207 g

Number or moles of $BaCl_2$

$$= \frac{\text{Number or moles of } BaCl_2}{\text{Molar mass of } BaCl_2}$$
$$= \frac{2}{207} = 9.6 \times 10^{-3}$$

Volume of solution = 400 cc = 0.4 L

Conductivity (κ) = 0.0058 ohm^{-1}cm^{-1}

$$\text{Molarity } (M) = \frac{\text{Moles}}{\text{Volume(L)}} = \frac{0.009}{0.4}$$

Molarity (M) = 0.024 M,

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(ii) What is the molar conductivity of the above solution?

ISC 2021-22 (Sem-I)

(a) 241.67 S cm^2/mol

(b) 261.47 S cm^2/mol

(c) 247.17 S cm^2/mol

(d) 361.47 S cm^2/mol

Ans : (a) 241.67 S cm^2/mol

$$\text{Molar conductivity} = \frac{\kappa \times 1000}{M}$$

$$\text{Molar conductivity} = \frac{0.0058\,\Omega^{-1}cm^{-1} \times 1000\,cm^3}{0.024\,mol}$$

$$\text{Molar conductivity} = 241.66\,S\,cm^2mol^{-1}$$

41. A conductivity cell is filled with 0.05 M NaOH solution offering a resistance of 31.6 ohm. If the cell constant of the cell is 0.367 cm^{-1}, calculate the following

(i) The value of specific conductance

(a) $1.29 \times 10^{-2}\,\Omega^{-1}cm^{-1}$

(b) $1.29 \times 10^{-3}\,\Omega^{-1}cm^{-1}$

(c) $1.16 \times 10^{-2}\,\Omega^{-1}cm^{-1}$

(d) $11.6 \times 10^{-2}\,\Omega^{-1}cm^{-1}$

Ans : (c) $1.16 \times 10^{-2}\,\Omega^{-1}cm^{-1}$

Molarity of solution = 0.05 M

Resistance of solution, $R = 31.6$ ohm

Cell constant of the cell = 0367 cm^{-1}

$$\text{Conductance} = \frac{1}{R} = \frac{1}{31.6}\,ohm^{-1}$$

Specific conductance

$$= \text{conductance} \times \text{cell constant}$$

$$= \frac{1}{31.6}\,ohm^{-1} \times 0.367\,cm^{-1}$$

$$= 0.0116\,ohm^{-1}cm^{-1}$$

$$= 1.16 \times 10^{-2}\,\Omega^{-1}cm^{-1}$$

(ii) The value of molar conductance

ISC 2021-22 (Sem-1)

(a) $232.20\,\Omega^{-1}\,cm^2\,mol^{-1}$

(b) $23.22\,\Omega^{-1}\,cm^2\,mol^{-1}$

(c) $119.07\,\Omega^{-1}\,cm^2\,mol^{-1}$

(d) $165.36\,\Omega^{-1}\,cm^2\,mol^{-1}$

Ans : (a) $232.20\,\Omega^{-1}\,cm^2\,mol^{-1}$

Molar conductance,

$$\Lambda_m = \frac{\kappa \times 1000\,cm^3}{\text{Molarity}}$$

$$= \frac{0.0116\,ohm^{-1}cm^{-1} \times 1000\,cm^3}{0.05\,mol}$$

$$= 232\,ohm^{-1}cm^2mol^{-1}$$

42. Assertion (A) Specific conductance of all electrolytes decreases on dilution.

Reason (R) On dilution, number of ions per unit volume decreases.

ISC Specimen 2023

(a) Both (A) and (R) are correct, and (R) is the correct explanation for (A).

(b) Both (A) and (R) are correct, but (R) is not the correct explanation for (A).

(c) (A) is correct but (R) is incorrect.

(d) (A) is incorrect but (R) is correct.

Ans : (a) Both (A) and (R) are correct, and (R) is the correct explanation for (A).

Specific conductance depends on the number of ions present per unit volume of the solution. On dilution, the volume of the solution increases, so the number of ions per unit volume decreases. Hence, the specific conductance of all electrolytes decreases on dilution.

43. Assertion (A) If a solution contains both H^+ and Na^+ions, the H^+ ions are reduced first at cathode.

Reason (R) Cations with higher E° value are reduced first at cathode.

ISC 2023

(a) Both (A) and (R) are correct and (R) is the correct explanation for (A).

(b) Both (A) and (R) are correct but (R) is not the correct explanation for (A).

(c) (A) is correct but (R) is incorrect.

(d) (A) is incorrect but (R) is correct.

Ans : (a) Both (A) and (R) are correct and (R) is the correct explanation for (A).

When a solution contain both H^+ and Na^+ ions H^+ ions are reduced first because E° for hydrogen is 0 V which is higher than $E^\circ_{(Na^+)} = -2.71$ V.

44. Assertion (A) : Molar conductivity of acetic acid increases sharply on dilution.

Reason (R) : Degree of ionisation of acetic acid increases on dilution.

ISC 2021

(a) Both A and R are true and R is the correct explanation of A

NODIA

(b) Both A and R are true but R is not the correct explanation of A

(c) A is true but R is false

(d) A is false but R is true

Ans : (b) Both A and R are true but R is not the correct explanation of A

Dilution increases ionisation of acetic acid and therefore molar conductivity increases sharply. However, increase in ionic mobility along with increased ionisation contributes to higher molar conductivity.

45. Assertion (A) : Zinc acts as anode in Daniell cell.

Reason (R) : Zinc has greater tendency to lose electrons than copper.

ISC 2024

(a) Both A and R are true and R is the correct explanation of A

(b) Both A and R are true but R is not the correct explanation of A

(c) A is true but R is false

(d) A is false but R is true

Ans : (c) A is true but R is false

Zinc acts as anode because it undergoes oxidation more readily. However, the reason is incorrect because zinc has lower reduction potential rather than merely "greater tendency" in an isolated sense.

46. Assertion (A) : Rusting of iron occurs faster in moist air than in dry air.

Reason (R) : Moisture acts as electrolyte during electrochemical corrosion.

ISC 2013

(a) Both A and R are true and R is the correct explanation of A

(b) Both A and R are true but R is not the correct explanation of A

(c) A is true but R is false

(d) A is false but R is true

Ans : (d) A is false but R is true

Moisture indeed behaves as an electrolyte and accelerates corrosion. However, rusting does not occur exclusively because of moisture; oxygen availability is also essential for electrochemical rust formation.

47. Assertion (A) : Lead storage battery can be recharged after use.

Reason (R) : Cell reactions in lead storage battery are reversible.

ISC 2008

(a) Both A and R are true and R is the correct explanation of A

(b) Both A and R are true but R is not the correct explanation of A

(c) A is true but R is false

(d) A is false but R is true

Ans : (b) Both A and R are true but R is not the correct explanation of A

Lead storage batteries are rechargeable because discharge products can be converted back into original reactants. The reversibility of reactions enables repeated charging and discharging cycles in secondary cells.

NODIA

48. Assertion (A) : Concentrated aqueous NaCl solution becomes basic during electrolysis.

Reason (R) : Sodium hydroxide is formed during electrolysis.

ISC 2004

(a) Both A and R are true and R is the correct explanation of A

(b) Both A and R are true but R is not the correct explanation of A

(c) A is true but R is false

(d) A is false but R is true

Ans : (c) A is true but R is false

During electrolysis of brine, OH^- ions accumulate in solution making it basic. Although NaOH is effectively formed in solution, the basicity mainly arises from increased hydroxide ion concentration.

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49. Electrolysis follows _____ .

ISC 2009

Ans :

Electrolysis follows Faraday's laws of electrolysis.

50. A galvanic cell converts _____ energy into _____ energy. (electrical/chemical)

ISC 2018

Ans :

chemical, electrical

51. In galvanic cell, electrons flow from _____ to _____through the connecting wires.

ISC 2013

Ans :

In galvanic cell, electrons flow from anode to cathode through the connecting wires.

52. Nernst equation is used for _____ cell.

ISC 2012

Ans :

Nernst equation is used for electrochemical cell.

53. Copper displaces _____ from its solution because it has a _____ reduction potential.

ISC 2002

Ans :

Copper displaces silver from its solution because it has a lower reduction potential.

54. The unit of conductance is _____ and that of specific conductance is _____ .

ISC 2016

Ans :

Siemen or Ω^{-1}, $\Omega^{-1}\text{cm}^{-1}$

55. The molar conductance of a solution _____ with dilution, while its specific conductance _____ with dilution.

ISC 2014

Ans :

The molar conductance of a solution increases with dilution, while its specific conductance decreases with dilution.

56. Kohlrausch's law is related to _____ .

ISC 2014

Ans :

Kohlrausch's law is related to infinite dilution.

57. Equivalent conductivity is the conducting power of all the ions furnished by one _____ of an electrolyte present in a definite _____ of the solution (volume, gram equivalent).

ISC 2020

Ans :

Gram equivalent, volume

58. The molar conductance of a solution _____ with dilution while its specific conductance _____ with dilution.

ISC Specimen 2018

Ans :

Increases, decreases.

59. The degree of dissociation of a weak electrolyte is _____ proportional to the _____ of its molar concentration.

ISC 2006

Ans :

The degree of dissociation of a weak electrolyte is inversely proportional to the square root of its molar concentration.

60. As concentration of an electrolytic solution increases, its _____ conductance increases but _____ conductance decreases.

ISC 2003

Ans :

As concentration of an electrolytic solution increases, its specific conductance increases but equivalent conductance decreases.

61. According to Faraday's law, one gram equivalent of ion is liberated by _____ .

ISC 2002

Ans :

According to Faraday's first law of electrolysis, one Faraday is the quantity of electricity required to deposit one gram equivalent of any substance.

Thus, one gram equivalent of ion is liberated by 96500 C.

ONE MARK QUESTIONS

62. What happens when a nickel rod is dipped into a copper sulphate solution? Justify your answer. ($E^{\circ}_{Ni^{2+}/Ni} = -0.25$ V and $E^{\circ}_{Cu^{2+}/Cu} = +0.34$ V).

ISC 2014

Ans :

Since, the standard electrode potential of Ni is less than that of Cu and possesses greater reducing power. So, nickel can displace copper from copper sulphate solution.

$$Cu^{2+}(aq) + Ni(s) \longrightarrow Ni^{2+}(aq) + Cu(s)$$

63. What is standard hydrogen electrode?

ISC 2014

Ans :

Standard Hydrogen Electrode (SHE) is an electrode in which H_2 gas at one atmospheric pressure is passed through a solution of H+ ions of 1 M concentration at 25°C placed in contact

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with Pt foil. This electrode is also called Normal Hydrogen Electrode (NHE). Its potential is taken as zero.

64. Two metallic elements A and B have the following standard potentials: $A = 0.40\ V$, $B = 0.80\ V$, What would you expect if element A was added to an aqueous salt solution of element B ? Give a reason for your answer.

ISC 2013

Ans :

Standard potential of $A < B$. Hence, A has more reducing power than B. So, when A is added to an aqueous salt solution of B, then B will form precipitate and A will form the salt displacing B from its solution.

65. Name the law or principle to which the following observations confirm: When 96500 coulombs of electricity is passed through a solution of copper sulphate, 3.175 g of copper is deposited on the cathode (At. wt. of Cu = 63.5).

ISC 2017, 2013

Ans :

Faraday's first law of electrolysis is confirmed from the given statement which states that 'the amount of substance deposited at a particular electrode as a result of electrolysis is directly proportional to the quantity of electricity passed'.

66. The reduction potential of a metal X is $-0.76\ V$ while that of Y is $-2.38\ V$. Which of the two metals is a stronger reducing agent? Give a reason for your answer.

ISC 2010

Ans :

Reduction potential of $X(-0.76\ V) < Y(-2.38\ V)$. Strong reducing agents have a large negative value. Hence, metal Y is a stronger reducing agent than metal X.

67. Arrange Ag, Cr and Hg metals in the increasing order of reducing power.

Given : $E^{o}_{Ag^{+}/Ag} = +0.80\ V$, $E^{o}_{Cr^{3+}/Cr} = -0.74\ V$

$E^{o}_{Hg^{2+}/Hg} = +0.79\ V$

ISC 2013

Ans :

Since, the standard potential values are in the order of

$E^{o}_{Cr^{3+}/Cr}(-0.74\ V) < E^{o}_{Hg^{2+}/Hg}(0.79\ V) < E^{o}_{Ag^{+}/Ag}(0.80\ V)$

i.e. arranged in the increasing order to gain electrons. To lose electron or to act as reducing agent, the order will be reverse,

i.e. $E^{o}_{Ag^{+}/Ag} < E^{o}_{Hg^{2+}/Hg} < E^{o}_{Cr^{3+}/Cr}$

68. Give a reason for the following.

Specific conductance decreases with dilution whereas equivalent conductance increases with dilution.

ISC 2007

Ans :

Specific conductance depends on number of ions per unit volume. On dilution, number of ions will decrease per unit volume.

Hence, specific conductance of the solution will decrease.

Equivalent conductance is the product of specific conductivity and volume of the solution containing one gram equivalent of the electrolyte.

As the decreasing value of specific conductivity is more than compensated by the increasing value of V, so the value of Λ_{eq} increases with dilution.

DIRECTION : Correct the following statement.

69. For a strong electrolyte, the plot of equivalent conductance versus concentration of the solution is a straight line.

ISC 2002

Ans :

For a strong electrolyte, the plot of molar conductance versus square root of concentration of solution is a straight line.

70. On dilution of a solution, its equivalent and specific conductance increases.

ISC 2001

Ans :

On dilution of a solution, its equivalent conductance increases and specific conductance decreases.

Copper displaces both zinc and silver from their solutions.

ISC 2000

Ans :

Zinc displaces both copper and silver from their solutions.

NODIA

72. Copper displaces only silver from the solution not zinc.

ISC 2014

Ans :

The reduction potential of three elements is in the order Zn< Cu< Ag. Hence, zinc is more reactive.

73. A student added a few drops of dilute sulphuric acid before electrolysing water. What was the purpose of adding the acid?

ISC 2022

Ans :

Dilute sulphuric acid increases the concentration of ions and improves electrical conductivity of water.

74. A zinc strip was connected as electrode in a Daniell cell and was found to dissolve gradually. What does this indicate about zinc?

ISC 2024

Ans :

It indicates that zinc undergoes oxidation and acts as the anode of the cell.

75. During an experiment, a student noticed that current stopped flowing when the salt bridge was removed from a galvanic cell. Why did this happen?

ISC 2002

Ans :

Removal of salt bridge disturbed electrical neutrality and interrupted the flow of ions in the cell.

76. A weak electrolyte showed a sudden rise in molar conductivity on dilution. What conclusion can be drawn about its ionisation?

ISC 2007

Ans :

Its degree of ionisation increases significantly on dilution.

77. A chemistry student used standard hydrogen electrode while measuring electrode potential of another electrode. Why was SHE selected?

ISC 2013

Ans :

Standard hydrogen electrode has zero electrode potential and serves as a reference electrode.

78. Iron objects near sea coasts rust faster than those in dry regions. What role does moisture play in this process?

ISC 2025

Ans :

Moisture acts as an electrolyte and accelerates electrochemical corrosion of iron.

79. During electrolysis of brine, the solution gradually became alkaline. Which substance caused this change?

ISC 2021

Ans :

Formation of sodium hydroxide made the solution alkaline.

80. Fuel cells are preferred in spacecraft despite their high cost. State one major advantage responsible for this preference.

ISC 2016, 2003

Ans :

Fuel cells are highly efficient and produce very little pollution.

81. A student diluted an electrolyte solution and observed decrease in conductivity. What caused this decrease?

ISC 2006

Ans :

The number of ions per unit volume decreased on dilution.

82. A silver spoon was coated with gold using electrolysis. Why was the spoon connected to cathode?

ISC 2013

Ans :

Metal deposition occurs at cathode during electroplating.

83. Copper ions were found to gain electrons in an electrochemical cell. What does this indicate about the copper electrode?

ISC 2022

Ans :

The copper electrode acts as cathode where reduction occurs.

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84. A metallic wire conducts electricity without undergoing chemical change, whereas an electrolyte does not. What causes this difference?
ISC 2011

Ans :
Metallic conduction occurs through electrons, whereas electrolytic conduction occurs through ions with chemical decomposition.

85. A galvanic cell stopped producing electricity after continuous use. What does this indicate about the cell reaction?
ISC 2021

Ans :
The cell reaction reached equilibrium and the EMF became zero.

86. Iron pipelines are often coated with zinc instead of copper. What is the advantage of using zinc coating?
ISC 2025

Ans :
Zinc provides sacrificial protection and prevents rusting of iron.

87. A discharged lead storage battery becomes functional again after charging. What property of the battery makes this possible?
ISC 2017

Ans :
Its chemical reactions are reversible.

88. Sodium metal was obtained during electrolysis of molten sodium chloride but not from aqueous sodium chloride. What is the reason?
ISC 2012, 2003

Ans :
In aqueous solution, water is reduced preferentially instead of sodium ions.

89. During electrolysis of concentrated sodium chloride solution, bubbles of chlorine gas appeared at one electrode. Which process produced this gas?
ISC 2024

Ans :
Oxidation of chloride ions produced chlorine gas.

90. Platinum is used in standard hydrogen electrode instead of copper. State one reason.
ISC 2005

Ans :
Platinum is chemically inert and does not participate in the reaction.

91. A student concluded that a cell reaction was spontaneous because its EMF was positive. What does positive EMF signify?
ISC 2001

Ans :
Positive EMF indicates that the reaction can occur spontaneously.

92. A strong electrolyte conducts electricity better than a weak electrolyte of same concentration. What causes this difference?
ISC 2014

Ans :
Strong electrolytes produce greater number of ions due to almost complete dissociation.

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TWO MARKS QUESTIONS

93. Why is platinum used in standard hydrogen electrode?
ISC 2023

Ans :
Platinum is chemically inert and does not take part in the electrode reaction. It also provides a porous surface for adsorption of hydrogen gas and facilitates transfer of electrons during the electrode process.

94. During electroplating, the article to be plated is connected as cathode. Explain.
ISC 2012

Ans :
Reduction occurs at cathode during electrolysis. Metal ions present in the electrolyte gain electrons at the cathode and get deposited as a thin metallic layer over the article connected to it.

95. Explain why conductivity decreases on dilution even though ionisation may increase.
ISC 2014

Ans :
Although dilution increases ionisation of electrolytes, it decreases the number of ions present per unit volume of solution. Due to lower ionic concentration, the ability of the solution to conduct electricity decreases and hence conductivity falls.

96. Explain why zinc acts as anode in a Daniell cell.
ISC 2004

Ans :
Zinc possesses lower reduction potential and greater tendency to lose electrons than copper. Therefore zinc undergoes oxidation by releasing electrons into the external circuit. Since oxidation occurs at anode, zinc acts as the anode in the Daniell cell.

97. During electrolysis of concentrated aqueous NaCl, the solution becomes alkaline. Explain.
ISC 2024

Ans :
During electrolysis, water molecules are reduced at cathode producing hydrogen gas and OH^- ions. These hydroxide ions remain in the solution along with Na^+ ions already present. Consequently sodium hydroxide is formed, making the solution alkaline in nature.

98. Why is a salt bridge necessary in a galvanic cell?
ISC 2002

Ans :
Salt bridge permits movement of ions between the two half-cells and maintains electrical neutrality. Without salt bridge, positive and negative charges would accumulate in the solutions, preventing further electron flow and stopping the functioning of the cell.

99. Explain why rusting of iron occurs faster in coastal regions.
ISC 2013, 2001

Ans :
Coastal regions contain high moisture and dissolved salts in air. Moisture acts as an electrolyte and salts increase electrical conductivity on iron surface. This accelerates electrochemical corrosion of iron, causing rusting to occur more rapidly than in dry regions.

100. Why are fuel cells considered superior to conventional cells in spacecraft?
ISC 2007

Ans :
Fuel cells are highly efficient and convert chemical energy directly into electrical energy. They produce water as the major product and cause very little pollution. They can also supply electricity continuously as long as fuel and oxygen are available.

101. A lead storage battery can be used repeatedly after recharging. Explain the reason.
ISC 2021

Ans :
The chemical reactions occurring during discharge of lead storage battery are reversible in nature. During charging, external electrical energy converts lead sulphate formed during discharge back into lead and lead dioxide, thereby restoring the battery for repeated use.

102. Why does copper electrode gain mass during electrolysis of $CuSO_4$ using copper electrodes?
ISC 2020

Ans :
Cu^{2+} ions present in the solution gain electrons at the cathode and get deposited as copper metal. Continuous deposition of copper on the electrode surface results in increase in mass of the copper electrode.

103. Explain why metals placed higher in electrochemical series are stronger reducing agents.
ISC 2003

Ans :
Metals placed higher in electrochemical series possess greater tendency to lose electrons and undergo oxidation easily. Since reducing agents donate electrons to other substances, these metals behave as strong reducing agents.

104. During electrolysis of molten NaCl, sodium metal is formed at cathode, whereas in aqueous NaCl solution hydrogen gas is obtained. Explain.
ISC 2025

Ans :
Molten NaCl contains only Na^+ and Cl^- ions, so sodium ions gain electrons at cathode to form sodium metal. In aqueous NaCl solution, water molecules are present and are reduced more easily than sodium ions. Hence hydrogen gas is liberated instead of sodium metal.

105. A galvanic cell stopped functioning after some time although electrodes remained intact. State the reason.
ISC 2017

Ans :
During operation of the galvanic cell, reactants gradually get consumed and products accumulate. As the reaction proceeds, the cell approaches

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equilibrium. At equilibrium, EMF becomes zero and electron flow through the external circuit stops, causing the cell to stop functioning.

106. Why does molar conductivity of weak electrolytes increase sharply on dilution?

ISC 2022

Ans :

Weak electrolytes are only partially ionised in concentrated solutions. On dilution, their degree of ionisation increases considerably according to Ostwald's dilution law. As more ions are produced in solution, the molar conductivity increases sharply with dilution.

107. A student observed that pure water did not conduct electricity effectively during electrolysis, but conduction improved after adding dilute sulphuric acid. Explain the reason.

ISC 2011

Ans :

Pure water undergoes very little ionisation and therefore contains only a small number of ions. Due to low ionic concentration, it conducts electricity poorly. Addition of dilute sulphuric acid increases the number of mobile ions such as H^+ and SO_4^{2-} ions, thereby increasing electrical conductivity and making electrolysis possible.

108. Define the following terms.

(i) Equivalent conductivity

(ii) Corrosion of metals

ISC 2018

Ans :

(i) **Equivalent conductivity** of a solution is defined as the conductance of all the ions produced from one gram equivalent of the electrolyte dissolved in V cm^3 of the solution when the distance between the electrodes is one cm and the area of electrodes is so large that whole of the solution is contained between them. It is represented by Λ_{eq}.

(ii) **Corrosion of metals** is basically an electrochemical phenomenon in which a metal oxide or other salt of the metal forms a coating on the metal surface, e.g. rusting of iron.

109. What is an electrochemical series? How is it useful in predicting whether a metal can liberate hydrogen from acid or not?

ISC 2018

Ans :

The arrangement of various standard half-cells in the order of their decreasing values of standard reduction potentials is called electrochemical series.

In the electrochemical series, metals that are placed above hydrogen are reactive metals and these reacts with acids like HCl (dil.), H_2SO_4 (dil.) to produce salt and hydrogen gas and have, placed below hydrogen.

$$\text{Metal} + \text{Dil. acid} \longrightarrow \text{Salt} + \text{Hydrogen}$$

$$\text{e.g. } \underset{\text{Zinc}}{Zn(s)} + \underset{\text{(Dil.)}}{2HCl(aq)} \longrightarrow \underset{\text{Zinc chloride}}{ZnCl_2(aq)} + \underset{\text{Hydrogen gas}}{H_2(g)} \uparrow$$

110. Define molar conductance of a solution. State its unit. How is it related to the specific conductance of a solution?

ISC 2013

Ans :

The conductance of that volume of solution which contains one mole of the solute and is placed between two parallel electrodes of 1 cm distance apart and having sufficient area to hold the whole of the solution is called its molar conductance.

It is denotes by Λ_m. If the concentration of a solution is C mol/L, then volume of the solution containing 1 mole of the electrolyte will be $1/C$ L or $1000/C$ cc.

Hence, Λ_m and κ can be related as $\Lambda_m = \dfrac{1000}{C} \times \kappa$, where, κ is specific conductance.

Its units are $ohm^{-1}cm^2mol^{-1}$ in CGS and $ohm^{-1}m^2mol^{-1}$ in SI system.

111. State Kohlrausch's law and give its mathematical expression mentioning the terms involved in it.

ISC 2010

Ans :

Kohlrausch's law states that the molar conductance of an electrolyte at infinite dilution is equal to the sum of the molar conductance of the two ions (cations and anions).'

$$\Lambda_m^\circ = \Lambda_+^\circ + \Lambda_-^\circ$$

where, Λ_+° and Λ_-° are the ionic conductivities of the cation and anion, respectively.

If an electrolyte furnishes more than one cation adn anion then, according to Kohlrausch's law,

$$\Lambda_m^\circ(A_mB_n) = m\Lambda_A^\circ + n\Lambda_B^\circ$$

where, m and n are the number of cations and anions per formula unit of electrolyte. Λ_A° and Λ_B° are the ionic conductivities of the ions A and B.

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THREE MARKS QUESTIONS

112. Explain the significance of positive EMF in an electrochemical cell.

ISC 2002

Ans :

Positive EMF indicates that the cell reaction occurs spontaneously.

In such a cell, oxidation and reduction reactions proceed naturally and chemical energy is converted into electrical energy. A positive EMF also signifies negative Gibbs free energy change for the reaction.

113. Explain why platinum is used in standard hydrogen electrode though it does not participate in the reaction.

ISC 2012

Ans :

Platinum is chemically inert and therefore does not interfere with the electrode reaction. It provides a porous surface for adsorption of hydrogen gas and facilitates transfer of electrons between hydrogen molecules and hydrogen ions in solution.

Thus platinum acts as an efficient conductor and catalyst in the standard hydrogen electrode.

114. Explain the advantages of hydrogen–oxygen fuel cell over ordinary cells.

ISC 2019, 2010

Ans :

Hydrogen–oxygen fuel cells are highly efficient because they directly convert chemical energy into electrical energy.

They are environmentally friendly since water is the only major product formed. They are also lightweight and can provide continuous electricity as long as hydrogen and oxygen are supplied.

115. Explain why metals with highly negative reduction potentials are more reactive.

ISC 2023

Ans :

Metals having highly negative reduction potentials possess greater tendency to lose electrons and undergo oxidation easily.

Since reactivity of metals depends upon ease of oxidation, such metals react readily with acids and other substances. Therefore they are considered highly reactive metals and strong reducing agents.

116. Describe the changes occurring during electrolysis of acidified water.

ISC 2021

Ans :

During electrolysis of acidified water, hydrogen ions gain electrons at cathode and form hydrogen gas.

At anode, water molecules lose electrons and produce oxygen gas.

Thus hydrogen gas is liberated at cathode, oxygen gas at anode and water decomposes into its constituent gases.

117. Explain why fuel cells are preferred in spacecraft and submarines.

ISC 2020

Ans :

Fuel cells are preferred because they are highly efficient and can operate continuously with regular fuel supply.

They produce water as a by-product, which can be used by astronauts. Fuel cells are also lightweight and produce very little environmental pollution.

118. Why does molar conductivity increase on dilution for both strong and weak electrolytes, but more sharply for weak electrolytes?

ISC 2018

Ans :

On dilution, ions move more freely due to decrease in interionic attraction, causing increase in molar conductivity for all electrolytes.

In weak electrolytes, dilution also increases degree of ionisation significantly, producing a much larger number of ions. Therefore weak electrolytes show a sharper increase in molar conductivity compared to strong electrolytes.

119. Explain the role of salt bridge in a galvanic cell. What would happen if it is removed?

ISC 2004

Ans :

Salt bridge maintains electrical neutrality by allowing migration of ions between the two half-cells. It also completes the internal circuit of the cell.

If the salt bridge is removed, positive and negative charges accumulate in the solutions. This prevents further electron flow through the external circuit and the cell stops functioning.

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120. Explain why hydrogen gas is liberated at cathode during electrolysis of aqueous NaCl solution instead of sodium metal.

ISC 2010

Ans :

In aqueous NaCl solution, both Na^+ ions and water molecules are present. Water has greater tendency to undergo reduction than Na^+ ions.

Therefore water molecules gain electrons and produce hydrogen gas at cathode instead of sodium metal being deposited.

121. Explain the working of a Daniell cell with suitable electrode reactions.

ISC 2024

Ans :

A Daniell cell consists of zinc electrode dipped in $ZnSO_4$ solution and copper electrode dipped in $CuSO_4$ solution connected through a salt bridge.

At anode, zinc undergoes oxidation:

$Zn \rightarrow Zn^{2+} + 2e^-$

At cathode, Cu^{2+} ions undergo reduction:

$Cu^{2+} + 2e^- \rightarrow Cu$

Electrons flow from zinc to copper through the external circuit, producing electric current.

122. During electrolysis of $CuSO_4$ solution using copper electrodes, concentration of the solution remains almost unchanged. Explain.

ISC 2016

Ans :

At cathode, Cu^{2+} ions gain electrons and get deposited as copper metal.

$Cu^{2+} + 2e^- \rightarrow Cu$

At anode, equal amount of copper dissolves into solution:

$Cu \rightarrow Cu^{2+} + 2e^-$

Thus Cu^{2+} ions removed from solution are replaced continuously, keeping concentration of $CuSO_4$ nearly constant.

123. Explain why rusting of iron is considered an electrochemical process.

ISC 2025

Ans :

Rusting occurs due to formation of tiny electrochemical cells on iron surface in presence of moisture and oxygen.

At anodic regions, iron undergoes oxidation:

$Fe \rightarrow Fe^{2+} + 2e^-$

At cathodic regions, oxygen undergoes reduction in presence of water. The Fe^{2+} ions finally form hydrated ferric oxide called rust.

124. Explain why lead storage battery is called a secondary cell.

ISC 2022

Ans :

Lead storage battery is called a secondary cell because its chemical reactions are reversible.

During discharge, lead and lead dioxide are converted into lead sulphate. On charging, external electrical energy reconverts lead sulphate back into original reactants.

Therefore the battery can be used repeatedly after recharging.

125. A student observed that conductivity decreases on dilution whereas molar conductivity increases. Explain the observation.

ISC 2015

Ans :

Conductivity depends on the number of ions present per unit volume of solution. On dilution, ionic concentration decreases and hence conductivity decreases.

Molar conductivity depends on total conductance produced by one mole of electrolyte. Due to greater ionic mobility and increased ionisation on dilution, molar conductivity increases.

126. Mention any two factors affecting the electrode potential of a metal.

ISC 2009

Ans :

Two factors affecting electrode potential of a metal are as follows

(i) **Position of the metal in electrochemical series**
More reactive the metal, greater is the tendency to lose electrons and hence, lower is the value of reduction potential of the metal. Thus, act as a strong reducing agent.

(ii) **Concentration of metal ions in the solution**
Dependence of the electrode potential of a metal on concentration of the electrolyte is given by Nernst equation.
For the electrode reaction,

$$M^{n+}(aq) + ne^- \longrightarrow M(s)$$

$$E_{M^{n+}/M} = E^{o}_{M^{n+}/M} + \frac{RT}{nF}\log_e \frac{[M^{n+}(aq)]}{[M(s)]}$$

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127. A student electrolysed concentrated aqueous sodium chloride solution and observed evolution of gases at both electrodes along with formation of an alkaline solution. Explain the reactions occurring during the process.

ISC 2007

Ans :

During electrolysis of concentrated aqueous NaCl solution, chloride ions are oxidised at the anode to form chlorine gas.

At cathode, water molecules are reduced to form hydrogen gas and OH^- ions.

The OH^- ions remain in solution along with Na^+ ions already present, resulting in formation of sodium hydroxide. Therefore the solution gradually becomes alkaline in nature.

FOUR MARKS QUESTIONS

128. Explain why molar conductivity of weak electrolytes increases sharply on dilution whereas conductivity decreases.

ISC 2025

Ans :

Conductivity depends upon the number of ions present per unit volume of solution. On dilution, ionic concentration decreases and therefore conductivity decreases.

Molar conductivity, however, depends upon conductance produced by one mole of electrolyte. In weak electrolytes, dilution increases degree of ionisation considerably, producing more ions.

Interionic attraction also decreases on dilution, increasing ionic mobility. Therefore molar conductivity increases sharply even though conductivity decreases.

129. Describe the electrochemical theory of rusting of iron.

ISC 2009

Ans :

Rusting of iron is an electrochemical process occurring in presence of moisture and oxygen. Tiny electrochemical cells are formed on the iron surface.

At anodic regions:

$Fe \rightarrow Fe^{2+} + 2e^-$

The electrons move to cathodic regions where oxygen is reduced:

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

Fe^{2+} ions combine with OH^- ions to form ferrous hydroxide, which is further oxidised to hydrated ferric oxide ($Fe_2O_3 \cdot xH_2O$), commonly known as rust.

Thus moisture and oxygen are essential for rust formation.

130. Explain the difference between metallic conductors and electrolytic conductors.

ISC 2019

Ans :

Metallic Conductors	Electrolytic Conductors
Conduct electricity through electrons	Conduct electricity through ions
No chemical change occurs	Chemical decomposition occurs
Conductivity decreases with rise in temperature	Conductivity increases with rise in temperature
Example : Cu, Ag	Example : HCl, NaOH

Thus metallic and electrolytic conduction differ in mechanism as well as behaviour.

131. Explain why zinc is used for sacrificial protection of iron.

ISC 2002

Ans :

Zinc possesses greater tendency to undergo oxidation than iron because it is placed higher in electrochemical series.

When zinc-coated iron is exposed to moisture, zinc acts as sacrificial anode and gets oxidised preferentially:

$Zn \rightarrow Zn^{2+} + 2e^-$

The electrons released protect iron from oxidation and rusting.

Even if the zinc coating is damaged, zinc continues to corrode instead of iron, thereby protecting the metal surface effectively.

132. Explain the significance of electrochemical series in predicting redox reactions.

ISC 2022, 2001

Ans :

Electrochemical series arranges electrodes according to increasing reduction potentials.

Metals higher in the series possess greater tendency to lose electrons and act as stronger reducing agents. Metals lower in the series are

NODIA

stronger oxidising agents.

Using electrochemical series:

1. Reactivity of metals can be compared
2. Spontaneity of reactions can be predicted
3. EMF of cells can be calculated
4. Oxidising and reducing powers can be determined

Thus electrochemical series is highly useful in studying redox behaviour.

133. Explain why conductivity decreases with dilution whereas molar conductivity increases.

ISC 2021

Ans :

Conductivity depends on the number of ions present per unit volume of solution. On dilution, ionic concentration decreases and therefore conductivity decreases.

Molar conductivity depends on conductance of ions produced by one mole of electrolyte. Due to increased ionic mobility and greater ionisation on dilution, molar conductivity increases.

For weak electrolytes, increase is much sharper because dilution greatly increases ionisation.

134. Explain the working of standard hydrogen electrode and state its importance.

ISC 2000

Ans :

Standard hydrogen electrode consists of platinum electrode coated with platinum black immersed in 1 M H^+ solution. Hydrogen gas at one atmospheric pressure is continuously bubbled over the electrode.

Electrode reaction:

$2H^+ + 2e^- \rightleftharpoons H_2$

The electrode can act both as anode and cathode depending upon the other half-cell connected.

Its standard electrode potential is assigned zero value. Therefore it is used as reference electrode for measuring standard electrode potentials of other electrodes.

135. Explain why electrolysis of $CuSO_4$ solution gives different products when inert electrodes and copper electrodes are used.

ISC 2016

Ans :

When inert electrodes are used:

1. Cu^{2+} ions are reduced at cathode forming copper metal.
2. Water is oxidised at anode producing oxygen gas.

When copper electrodes are used:

1. Cu^{2+} ions are reduced at cathode depositing copper.
2. Copper anode dissolves forming Cu^{2+} ions.

Thus with copper electrodes, concentration of $CuSO_4$ remains almost constant, whereas with inert electrodes oxygen gas is evolved and concentration changes gradually.

136. Explain the importance of salt bridge in maintaining the working of an electrochemical cell.

ISC 2025

Ans :

During operation of an electrochemical cell, oxidation at anode increases positive ion concentration while reduction at cathode decreases positive ion concentration.

Salt bridge permits migration of ions:

1. Anions move towards anode
2. Cations move towards cathode

This maintains electrical neutrality in both half-cells and completes the internal circuit.

Without salt bridge, charge accumulation would stop electron flow and the cell would cease to operate.

137. Explain why metals with highly negative reduction potentials are considered strong reducing agents.

ISC 2010

Ans :

Reduction potential measures tendency of a substance to gain electrons. Metals having highly negative reduction potentials possess very low tendency to gain electrons and very high tendency to lose electrons.

Therefore such metals undergo oxidation readily:

$M \rightarrow M^{n+} + ne^-$

Since reducing agents donate electrons to other substances, these metals behave as strong reducing agents and show high chemical reactivity.

138. A student electrolysed concentrated aqueous sodium chloride solution using inert electrodes. Explain the reactions occurring at both electrodes and justify why the solution becomes alkaline after electrolysis.

ISC 2023

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Ans :

During electrolysis of concentrated aqueous sodium chloride solution, both Na^+ and H_2O are present near the cathode. Water is preferentially reduced and hydrogen gas is liberated.

At cathode:

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

At anode, chloride ions undergo oxidation:

$2Cl^- \rightarrow Cl_2 + 2e^-$

The OH^- ions produced at cathode remain in solution along with Na^+ ions already present. As a result, sodium hydroxide is formed and the solution gradually becomes alkaline in nature.

The overall reaction is:

$2NaCl + 2H_2O \rightarrow 2NaOH + H_2 + Cl_2$

139. Explain the construction and working of a Daniell cell. Why is the salt bridge essential for its functioning?

ISC 2017

Ans :

A Daniell cell consists of zinc electrode dipped in $ZnSO_4$ solution and copper electrode dipped in $CuSO_4$ solution. The two solutions are connected through a salt bridge and the electrodes are connected externally through a wire.

At anode, zinc undergoes oxidation:

$Zn \rightarrow Zn^{2+} + 2e^-$

At cathode, Cu^{2+} ions gain electrons:

$Cu^{2+} + 2e^- \rightarrow Cu$

Electrons flow from zinc to copper through the external circuit, producing electric current.

The salt bridge maintains electrical neutrality by allowing migration of ions between the two half-cells. Without salt bridge, charge accumulation would stop electron flow and the cell would cease to function.

140. Explain the construction and working of lead storage battery. Why is it called a secondary cell?

ISC 2002

Ans :

A lead storage battery consists of lead plates as anode, lead dioxide plates as cathode and dilute sulphuric acid as electrolyte.

During discharge:

At anode:

$Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^-$

At cathode:

$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$

Both electrodes gradually become coated with $PbSO_4$.

During charging, external electrical energy reverses these reactions and regenerates Pb and PbO_2.

Since the cell reactions are reversible and the battery can be recharged repeatedly, it is called a secondary cell.

141. Explain Faraday's first and second laws of electrolysis.

ISC 2005

Ans :

Faraday's first law states that the mass of substance deposited during electrolysis is directly proportional to the quantity of electricity passed.

$$W \propto Q$$

or $$W = ZIt$$

where Z is electrochemical equivalent.

Faraday's second law states that when same quantity of electricity is passed through different electrolytes connected in series, the masses of substances deposited are proportional to their equivalent masses.

Thus electrolysis depends directly upon the quantity of electricity passed through the electrolyte.

142. Explain the principle and advantages of hydrogen–oxygen fuel cell.

ISC 2024

Ans :

In a hydrogen–oxygen fuel cell, hydrogen gas is supplied at anode and oxygen gas at cathode in presence of alkaline electrolyte.

At anode:

$2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$

At cathode:

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

Overall reaction:

$2H_2 + O_2 \rightarrow 2H_2O$

The cell converts chemical energy directly into electrical energy.

Advantages:

1. High efficiency
2. Environmentally clean
3. Lightweight
4. Continuous electricity generation as long as fuel is supplied

NODIA

NUMERICAL QUESTIONS

143. Calculate the molar conductance at infinite dilution (Λ_m°) for NH_4OH. Given that Λ_m° for $Ba(OH)_2$, $BaCl_2$ and NH_4Cl are $457\ ohm^{-1}\,cm^2\,mol^{-1}$, $240\ ohm^{-1}\,cm^2\,mol^{-1}$ $129\ ohm^{-1}\,cm^2\,mol^{-1}$ respectively.

ISC 2011

Ans :

As we know that,

$$\lambda^\circ_{m(NH_4OH)} = \lambda^\circ_{m(Ba(OH)_2)} + \lambda^\circ_{m(NH_4Cl)} - \lambda^\circ_{m(BaCl_2)}$$
$$= 457 + 129 - 240$$
$$= 346\ ohm^{-1}cm^2mol^{-1}$$

144. Calculate the number of coulombs required to deposit 5.4 g of Al, when the electrode reaction is

$$Al^{3+} + 3e^- \longrightarrow Al$$

[Atomic weight of Al = 27g/mol]

ISC 2016

Ans :

$$Al^{3+} + 3e^- \longrightarrow Al$$

For 27 g (1 mol) of Al required $= 3 \times 96500\ C$

$$1\text{ g of Al required} = \frac{3 \times 96500}{27}\ C$$

$$5.4\text{ g of Al required} = \frac{3 \times 96500}{27} \times 5.4$$
$$= 57900\ C$$

Thus, the number of coulombs required to deposit 5.4 g Al is 57900 C.

145. How many hours does it take to reduce 3 moles of Fe^{3+} to Fe^{2+} with 2.0 A current intensity?

ISC 2016

Ans :

$$\text{Current} = 2\ A$$
$$\text{Number of moles of iron} = 3\ mol$$

From number of moles,

$$\text{Weight of iron} = 3 \times 55.8 = 168\ g$$

From Faraday's equation, $w = ZIt$

$$t = \frac{168 \times 96500}{56 \times 2 \times 3600}$$
$$t = 40.2\ h$$

146. Specific conductivity of 0.20 M solution of KCl at 298 K is 0.025 S cm^{-1}. Calculate its molar conductivity.

ISC 2017

Ans :

Specific conductivity $(\kappa) = 0.025\ S\,cm^{-1}$

Concentration $(C) = 0.20$ M-

Now, molar conductivity

$$(\Lambda_m) = \frac{1000}{C} \times \kappa$$
$$= \frac{1000}{0.2} \times 0.025 = 125\ S\,cm^2\,mol^{-1}$$

147. Calculate the equivalent conductivity of 1 M H_2SO_4 whose specific conductivity is $26 \times 10^{-2}\ ohm^{-1}\,cm^{-1}$.

ISC 2006

Ans :

Given, concentration, $C = 1\ M,$

$$= 1 \times 2\ M = 2\ M$$

Specific conductivity, $\kappa = 26 \times 10^{-2}\ \Omega^{-1}cm^{-1}$

Equivalent conductance, $\Lambda_{eq} = \frac{1000}{1 \times 2} \times 26 \times 10^{-2}$

$$= 130\ S\,cm^2\,equiv^{-1}$$

148. The conductivity of 0.2 M KCl solution is $3 \times 10^{-2}\ ohm^{-1}\,cm^{-1}$. Calculate its molar conductance.

ISC 2012

Ans :

Given, C for KCl $= 0.2\ M,$

$$\kappa = 3 \times 10^{-2}\ \Omega^{-1}cm^{-1}$$
$$\Lambda_m = \frac{1000}{0.2} \times 3 \times 10^{-2}$$
$$= \frac{30}{0.2}$$
$$= 1.5 \times 10^2\ \Omega^{-1}cm^2mol^{-1}$$

149. Calculate the number of coulombs of charge required to deposit 24.35 g of aluminium from a solution containing Al^{3+} ions.

(Atomic weight of Al = 27)

ISC Specimen 2021

Ans :

$$Al^{3+} + 3e^- \longrightarrow Al$$
$$3\ mol\ e^- \longrightarrow 27\ g\ of\ Al$$
$$24.35\ g \longrightarrow \frac{3}{27} \times 24.35$$
$$= 2.70\ mole\ of\ e^-$$
$$\text{Number of } F = \frac{Q}{96500} = 2.70$$
$$Q = 2.70 \times 96500 = 26550\ C$$

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150. The molar conductivity of NaCl, CH_3COONa and HCl at infinite dilution is 126.45, 91.0 and 426.16 $ohm^{-1}\,cm^2\,mol^{-1}$ respectively.Calculate the molar conductivity (λ°_m) for CH_3COOH at infinite dilution.

ISC 2020

Ans :

Given, $\Lambda^\circ_{NaCl} = 126.45\ ohm^{-1}cm^2mol^{-1}$

$\Lambda^\circ_{CH_3COONa} = 91.0\ ohm^{-1}cm^2mol^{-1}$

$\Lambda^\circ_{HCl} = 426.16\ ohm^{-1}cm^2mol^{-1}$

$\Lambda^\circ_{CH_3COOH} = \Lambda^\circ_{CH_3COONa} + \Lambda^\circ_{HCl} - \Lambda^\circ_{NaCl}$

$= (91.0 + 426.16) - 126.45$

$= 390.71\ ohm^{-1}cm^2mol^{-1}$

151. 0.05 M NaOH solution offered a resistance of 31.6 Ω in a conductivity cell at 298 K. If the cell constant of the cell is $0.367\ cm^{-1}$, calculate the molar conductivity of the NaOH solution.

ISC 2014

Ans :

Concentration, $C = 0.05\,M$,

Resistance, $R = 31.6\,\Omega$

Cell constant $= 0.367\ cm^{-1}$

$\kappa = \frac{0.367}{31.6}\,\Omega^{-1}cm^{-1}$

$\Lambda_m = \frac{1000}{C} \times \kappa = \frac{1000}{C} \times \frac{G^*}{R}$

$\Lambda_m = \frac{1000}{0.05} \times \frac{0.367}{31.6}$

$= 232.278\,\Omega^{-1}cm^2mol^{-1}$

152. A conductivity cell has a cell constant of $0.5\ cm^{-1}$. This cell when filled with 0.01 M sodium chloride solution has a resistance of 384 Ω at 25° C. Calculate the equivalent conductivity of 0.01 M sodium chloride at 25° C.

ISC 2025

Ans :

Given, cell constant $= 0.5\ cm^{-1}$,

Concentration, $C = 0.01\,M$, $R = 384\,\Omega$

Equivalent conductance,

$\Lambda_{eq} = \frac{1000}{0.01} \times \kappa = \frac{1000}{0.01} \times \frac{G^*}{R}$

$= \frac{1000}{0.01} \times \frac{0.5}{384}$

(For NaCl, 0.01 M = 0.01 N)

$= 130.2\,\Omega^{-1}cm^2equiv^{-1}$

153. Calculate the emf of the following cell reaction at 298 K :

$Mg(g) + Cu^{2+}(0.0001M)\,Mg^{2+}(0.001M) + Cu(s)$

The standard potential (E°) of the cell is 2.71 V.

ISC 2015

Ans :

$Mg(g) + Cu^{2+}(0.0001\,M) \longrightarrow Mg^{2+}(0.001\,M) + Cu(s)$

Standard electrode potential = 2.71 V

$E = E^\circ_{cell} - \frac{0.0591}{n}\log\frac{[Mg^{2+}]}{[Cu^{2+}]}$

$E = 2.71 - \frac{0.0591}{2}\log\frac{0.001}{0.0001}$

$= 2.71 - \frac{0.0591}{2}\log 10$

$E = 2.71 - 0.02955 = 2.68\ V$

154. The specific conductance of 2.5×10^4 M formic acid is $5.25 \times 10^{-5}\ ohm^{-1}cm^{-1}$. Calculate its molar conductivity and degree of dissociation.

Given : $\lambda^\circ_{(H^+)} = 349.5\ ohm^{-1}\,cm^2\,mol^{-1}$

and $\lambda^\circ_{(HCOO^-)} = 50.5\ ohm^{-1}\,cm^2\,mol^{-1}$

ISC 2002

Ans :

As we know that,

$\Lambda_m = \frac{\kappa \times 1000}{C}$ $(\Omega^{-1}cm^{-1} = s)$

$= \frac{5.25 \times 10^{-5}\,\Omega^{-1}cm^{-1} \times 1000}{2.5 \times 10^{-4}\,mol\,cm^{-3}}$

$= 210\,S\,cm^2mol^{-1}$

$\Lambda^\circ_{(HCOOH)} = \Lambda^\circ_{(HCOO^-)} + \Lambda^\circ_{H^+}$

$= 50.5 + 349.5 = 400\,S\,cm^2mol^{-1}$

$\alpha = \frac{\Lambda_m}{\Lambda^\circ_m} = \frac{210}{400} = 0.52$ or 52%

155. Calculate the time taken to deposit 1.27 g of copper at cathode when a current of 2 amp, is passed through the solution of $CuSO_4$.
(Atomic weight of Cu = $63.5\ g\ mol^{-1}$)

ISC 2013

Ans :

Reaction taking place is

$Cu^{2+} + 2e^- \longrightarrow Cu\ (n = 2)$

By Faraday's first law,

$W = ZQ \Rightarrow Zit$

Where, $w =$ amount deposit, $i =$ current and $t =$ time

$Z = \frac{\text{atomic weight}}{\text{no. of } e^- \times F}$

NODIA

So, we get $1.27 = \frac{63.5 \times 2 \times t}{2 \times 96500}$

$$t = \frac{96500 \times 1.27}{63.5} = 1930\ \text{s}$$

156. Calculate the degree of dissociation (α) of acetic acid, if its molar conductivity (Λ_m) is $39.05\ \text{S cm}^2\ \text{mol}^{-1}$.
(Given : $\lambda^o_{(H^+)} = 349.6\ \text{S cm}^2\ \text{mol}^{-1}$ and $\lambda^o_{(CH_3COO^-)} = 40.95\ \text{S cm}^2\ \text{mol}^{-1}$)

ISC 2020

Ans :

Given, $\Lambda_m = 39.05\ \text{S cm}^2\text{mol}^{-1}$

Degree of dissociation

$$(\alpha) = \frac{\Lambda_m}{\Lambda^o_m}$$

$$\lambda^o_{CH_3COOH} = \lambda^o_{CH_3COO^-} + \lambda^o_{H^+}$$

$$\Lambda^o_{CH_3COOH} = 40.95 + 349.6$$

$$= 390.55\ \text{S cm}^2\text{mol}^{-1}$$

Now, $\alpha = \frac{39.05}{390.55} = 0.099$

157. Calculate the mass of silver deposited at cathode when a current of 2 amperes is passed through a solution of $AgNO_3$ for 15 min.
(At. wt. of Ag = 108, 1 F = 96500 C)

ISC 2019

Ans :

Given, current $(i) = 2$ amperes.

time $(t) = 15\ \text{min}$

$$= 15 \times 60 = 900\ \text{s}$$

$$Q = i \times t$$

$$= 2 \times 900 = 1800\ \text{C}$$

and atomic mass of Ag = 108

96500 C deposit silver (Ag) = 108 g

1800 C deposit silver (Ag)

$$= \frac{108 \times 1800}{96500} = 2.01\ \text{g}$$

Hence, silver deposited = 2.01 g

158. A 0.05 M NaOH solution offered a resistance of $31.6\ \Omega$ in a conductivity cell. If the cell constant of the conductivity cell is $0.378\ \text{cm}^{-1}$, determine the molar conductance of NaOH solution at this temperature.

ISC 2008

Ans :

Given, concentration,

$$C = 0.05\ \text{M},$$

Resistance $(R) = 31.6\ \Omega,$

Cell constant $(G^*) = 0.378\ \text{cm}^{-1}$

$$\kappa = \frac{\text{Cell constant}}{\text{Resistance}}$$

$$= \frac{0.378}{31.6}\ \Omega^{-1}\text{cm}^{-1}$$

Molar conductance,

$$\Lambda_m = \frac{1000}{0.05} \times \frac{0.378}{31.6}$$

$$= 239.24\ \Omega^{-1}\text{cm}^2\text{mol}^{-1}$$

159. How many electrons will flow when a current of 5 A is passed through a solution for 200 s ?

ISC 2011

Ans :

Given, current, $i = 5\ \text{A}$

and time, $t = 200\ \text{s}$

Amount of charge, $Q = it$

(from Faraday's first law)

$$= 5 \times 200 = 1000\ \text{C}$$

96500 C of electric charge is carried by 6.0×10^{23} electrons.

1000 C of electric charge is carried by

$$= \frac{6.0 \times 10^{23}}{96500} \times 1000$$

$$= \frac{6000 \times 10^{23}}{96500}$$

$$= 6.217 \times 10^{21}\ \text{electrons}$$

160. Calculate the maximum work that can be obtained from the given electrochemical cell constructed with two metals M and N.
$(E^o_{M^{2+}/M} = -0.76, E^o_{N^{2+}/N} = +0.34\ \text{V})$
The cell reaction is $M + N^{2+} \longrightarrow M^{2+} + N$

ISC 2012

Ans :

Given, $E^o_{M^{2+}/M} = 0.76\ \text{V}$, $E^o_{N^{2+}/N} = +0.34\ \text{V}$

So, $n = 2$

For the cell

At cathode, $N^{2+} + 2e^- \longrightarrow N$

At anode, $M \longrightarrow M^{2+} + 2e^-$

$$E^o_{cell} = E^o_{cathode} - E^o_{anode}$$

$$= 0.34 - (-0.76) = 1.1\ \text{V}$$

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$$W_{max} = -nFE^{o}_{cell}$$
$$= -2 \times 96500 \times 1.1 (1\,F = 96500\,C)$$
$$= -212300\,J$$
$$= -212.3\,kJ$$

161. Calculate the emf and ΔG for the cell reaction at 298 K.

$Mg(s)\,|\,Mg^{2+}(0.1\,M)\,||\,Cu^{2+}(0.01\,M)\,|\,Cu(s)$

Given, $E^{o}_{cell} = 2.71\,V$ $1\,F = 96500\,C$

ISC 2019

Ans :

$$\Delta G^{\circ} = -nFE^{o}_{cell}$$

Where, n = no. of electrons participate = 2

Given, $E^{o}_{cell} = 2.71\,V$ = emf of cell

$F = 96500\,C$

$$\Delta G = -2 \times 96500 \times 2.71$$
$$= -523030\,J\,mol^{-1}$$
$$\Delta G = -523.030\,kJ/mol$$

Now, $$E_{cell} = E^{o}_{cell} - \frac{0.0591}{n}\log\frac{[Mg^{2+}]}{[Cu^{2+}]}$$
$$= 2.71 - \frac{0.0591}{2}\log\frac{[0.1]}{[0.01]}$$
$$= 2.71 - 0.02955 = 2.68045$$

EMF of cell = 2.68045

162. Write the Nernst equation for the cell reaction given below and calculate the emf of the cell at 298 K.

ISC Specimen 2023

$2Cr(s) + 3Fe^{2+}(0.1\,M) \longrightarrow 2Cr^{3+}(0.01\,M) + 3Fe(s)$

Given : $E^{o}_{(Cr^{3+}/Cr)} = -0.74\,V$, $E^{o}_{(Fe^{2+}/Fe)} = -0.44\,V$

Ans :

The emf of cell is given by

$$E^{o}_{cell} = E^{o}_{cathode} - E^{o}_{anode}$$
$$= E^{o}_{Fe^{2+}/Fe} - E^{o}_{Cr^{3+}/Cr}$$
$$= -0.44 - (-0.74) = 0.30\,V$$

The Nernst equation is formulated as

$$E_{cell} = E^{o}_{cell} - \frac{0.0591}{n}\log\frac{M^{n+}}{M}$$
$$= 0.30 - \frac{0.0591}{6}\log\frac{(0.01)^2}{(0.1)^3}$$
$$= 0.30 + \frac{0.0591}{6} = 0.30985\,V$$

163. Calculate E_{cell} at 25° C for the reaction,

$Zn + Cu^{2+}(0.20\,M) \longrightarrow Zn^{2+}(0.50\,M) + Cu$

Given : $E^{o}_{(Zn^{2+}/Zn)} = -0.76\,V$;

$E^{o}_{(Cu^{2+}/Cu)} = 0.34\,V$

ISC 2007

Ans :

Given, $\underset{(0.20\,M)}{Zn + Cu^{2+}} \longrightarrow \underset{(0.50\,M)}{Zn^{2+}} + Cu$

$Zn \longrightarrow Zn^{2+} + 2e^{-}$;

$(E^{o}_{Zn^{2+}/Zn}) = -0.76\,V$

$Cu^{2+} + 2e^{-} \longrightarrow Cu$;

$(E^{o}_{Cu^{2+}/Cu}) = 0.34\,V$

Hence, $n = 2$

$$E^{o}_{cell} = E^{o}_{cathode} - E^{o}_{anode}$$
$$= 0.34 - (-0.76) = 1.10\,V$$
$$E_{cell} = E^{o}_{cell} - \frac{0.059}{n}\log_{10}\frac{[Zn^{2+}]}{[Cu^{2+}]}$$

Putting values in Nernst equation

$$E_{cell} = 1.10 - \frac{0.059}{2}\log\frac{(0.50)}{(0.20)}$$
$$= 1.088\,V$$

164. 0.3605 g of a metal is deposited on the electrode by passing 1.2 A of current for 15 min through a salt solution. The atomic weight of the metal is 96. What is the valency of metal ?

ISC 2014

Ans :

Amount of metal,

$w = 0.3605\,g$,

Current, $i = 1.2\,A$,

Time, $t = 15\,min = 15 \times 60\,s$

$$0.3605 = \frac{E}{96500} \times 1.2 \times 15 \times 60$$

(where, E is equivalent weight of metal)

$$E = \frac{0.3605 \times 96500}{1.2 \times 15 \times 60} = 32.211$$
$$E = 32.21$$
$$\text{Equivalent weight} = \frac{\text{Atomic weight}}{\text{Valency}}$$
$$\text{Valency} = \frac{96}{32.21} = 2.98 \cong 3$$

(As atomic weight of metal is 96)

Hence, valency of metal = 3

NODIA

165. Calculate the standard free energy change (ΔG°) for the following chemical reaction.

ISC Specimen 2023

$Cd(s) + 2Ag^+ \longrightarrow Cd^{2+} + 2Ag(s)$

$E^\circ_{Cd^{2+}/Cd} = -0.40\ V,\ E^\circ_{Ag^+/Ag} = +0.80\ V$

Ans :

The standard Gibbs energy is given by formula

$$\Delta G = -nFE^\circ_{cell}$$

Where, n = no. of electrons lost of gained

F = Faraday's constant = 96500 C

E° = EMF of cell

At cathode, $Cd \longrightarrow Cd^{2+} + 2e^-$

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$
$$= 0.80 - (-0.40) = 1.20$$

According to reaction given the change in oxidation state $(n) = 2$

$$\Delta G = -2 \times 96500(1.20)$$
$$= -231600\ J$$
$$= -231.6\ kJ$$

166. Calculate emf of the following cell at 298 K.

$Mg(s)\,|\,Mg^{2+}(0.1\ M)\,||\,Cu^{2+}(0.01\ M)\,|\,Cu(s)$

[Given : $E^\circ_{cell} = +2.71\ V$ 1 Faraday $= 96500\ C\ mol^{-1}$]

ISC Specimen 2018

Ans :

For the given cell, the half-cell reactions will be given as below:

At anode, $Mg \longrightarrow Mg^{2+} + 2e^-$

At cathode, $Cu^{2+} + 2e^- \longrightarrow Cu$

Therefore, the overall cell reaction will be

$$Mg + Cu^{2+} \longrightarrow Mg^{2+} + Cu$$

According to the Nernst equation, we get

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n}\log\left[\frac{Mg^{2+}}{Cu^{2+}}\right]$$

In this case, $n = 2$

$$E_{cell} = 2.71 - \frac{0.0591}{2}\log\left[\frac{0.1}{0.01}\right]$$
$$= 2.71 - 0.0295\log 10$$
$$= 2.71 - 0.0295$$
$$E_{cell} = 2.68\ V$$

167. A solution of 0.1 N KCl offers a resistance of 245 Ω. Calculate the specific conductance and the equivalent conductance of the solution if the cell constant is $0.571\ cm^{-1}$.

ISC 2025

Ans :

Given, $R = 245\ \Omega$,

Cell constant $= 0.571\ cm^{-1}$

Hence,

$$\text{specific conductance} = \frac{\text{Cell constant}}{\text{Resistance}}$$
$$\kappa = \frac{0.571}{245} = 0.00233\ \Omega^{-1}cm^{-1}$$
$$= 2.33 \times 10^{-3}\ \Omega^{-1}cm^{-1}$$

Equivalent conductance

$$\Lambda_{eq} = \frac{1000}{C} \times \kappa$$

Concentration, $C = 0.1\ N$

$$\Lambda_{eq} = \frac{1000}{0.1} \times 2.33 \times 10^{-3}$$
$$= 23.3\ \Omega^{-1}cm^2equiv^{-1}$$

168. Calculate the value of E_{cell} at 298 K for the following cell : $Al\,|\,Al^{3+}(0.01\ M)\,||\,Sn^{2+}(0.015\ M)\,|\,Sn$

Given : $E^\circ_{Al^{3+}/Al} = -1.66\ V$ and $E^\circ_{Sn^{2+}/Sn} = -0.14\ V$

ISC 2013

Ans :

Given, $E^\circ_{Al^{3+}/Al} = -1.66\ V$

and $E^\circ_{Sn^{2+}/Sn} = -0.14\ V$

At anode, $\left.\begin{matrix} Al \longrightarrow Al^{3+} + 3e^- \end{matrix}\right]\times 2$

$\left.\begin{matrix} Sn^{2+} + 2e^- \longrightarrow Sn \end{matrix}\right]\times 3$

$n = 6$

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$
$$= -0.14 - (-1.66)$$
$$= -0.14 + 1.66$$
$$= 1.52\ V$$

$$E_{cell} = E^\circ_{cell} - \frac{0.059}{n}\log\frac{[Al^{3+}]^2}{[Sn^{2+}]^3}$$
$$= 1.52 - \frac{0.059}{6}\log\frac{(0.01)^2}{(0.015)^3}$$
$$= 1.52 - \frac{0.059}{6} \times 1.47$$
$$= 1.52 - 0.0144$$
$$= 1.5055\ V$$

169. Calculate the emf and ΔG° for the cell reaction at 25° C.

$$\underset{(0.1\,M)}{Zn(s)\,|\,Zn^{2+}(aq)}\,||\,\underset{(0.01\,M)}{Cd^{2+}(aq)}\,|\,Cd(s)$$

Given, $E^\circ_{Zn^{2+}/Zn} = -0.763$ and $E^\circ_{Cd^{2+}/Cd} = -0.403$ V

ISC 2018

Ans :

The cell reaction is

$$Zn(s) + Cd^{2+}(aq) \longrightarrow Cd(s) + Zn^{2+}(aq)$$

E°_{cell} of the cell is given by

$$E^\circ_{cell} = E^\circ_{right} - E^\circ_{left}$$
$$= -0.403 - (-0.763) = 0.36\ V$$

Applying Nernst equation to the cell reaction

$$E_{cell} = E^\circ_{cell} - \frac{0.059}{n}\log\frac{[Zn^{2+}(aq)]}{[Cd^{2+}(aq)]}$$
$$E_{cell} = 0.36 - \frac{0.059}{2}\log\frac{0.1}{0.01} \qquad (n=2)$$
$$E_{cell} = 0.36 - 0.0295\log 10$$
$$= 0.36 - 0.0295 \times 1 = 0.3305\ V$$

Now, $\Delta_r G^\circ = -nFE^\circ_{cell}$

$$= -2 \times 96500 \times 0.33$$
$$= -63690\ J\ mol^{-1}$$
$$= -63.69\ kJ\ mol^{-1}$$

170. The resistance of a conductivity cell containing 0.001 M KCl solution at 298 K is 1500 ohm. What is the cell constant and molar conductivity of 0.001 M KCl solution, if the conductivity of this solution is 0.146×10^{-3} ohm^{-1} cm^1 at 298 K ?

ISC 2019

Ans :

Concentration (C) of KCl solution $= 0.001$ M

Resistance (R) of 0.001 M KCl $= 1500\,\Omega$

Conductivity (κ) at 298 K of KCl solution

$$= 0.146 \times 10^{-3}\,\Omega^{-1}cm^{-1}$$

Also, $\kappa(\text{Kappa}) = \frac{1}{R} \times \frac{l}{a}$

where, $\frac{l}{a}$ = cell constant

$$\frac{l}{a} = \kappa(\text{Kappa}) \times R$$
$$= 0.146 \times 10^{-3} \times 1500$$

Cell constant $= 219 \times 10^{-3}\ cm^{-1}$

and Λ_m (molar conductivity)

$$= \frac{\kappa \times 1000}{C}$$
$$= \frac{0.146 \times 10^{-3} \times 1000}{0.001}$$
$$= 146\ S\ cm^2 mol^{-1}$$

Hence, cell constant $= 219 \times 10^{-3}\ cm^{-1}$

Molar conductivity $= 146\ S\ cm^2\ mol^{-1}$

171. Calculate the emf of the following cell at 298 K.

$Cu\,|\,Cu^{2+}(0.025\,M)\,||\,Ag^+(0.005\,M)\,|\,Ag$

Given, $E^\circ_{Cu^{2+}/Cu} = 0.34$ V, $E^\circ_{Ag^+/Ag} = 0.80$ V

1 Faraday $= 96500\ C\ mol^{-1}$

ISC 2023

Ans :

At cathode,

$[Ag^+ + e^- \longrightarrow Ag] \times 2;$

$$E^\circ_{Ag^+/Ag} = 0.80\ V \qquad ...(i)$$

At anode, $Cu \longrightarrow Cu^{2+} + 2e;$

$$E^\circ_{Cu/Cu^{2+}} = -0.34\ V \qquad ..(ii)$$

Overall equation,

$2Ag^+ + Cu \longrightarrow Cu^{2+} + 2Ag$

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$
$$= 0.80 - 0.34 = 0.46\ V$$

Applying Nernst equation,

$$E = E^\circ - \frac{0.0591}{n}\log\frac{[Cu^{2+}][Ag]^2}{[Ag^+]^2[Cu]}$$
$$= E^\circ - \frac{0.0591}{n}\log\frac{[Cu^{2+}]}{[Ag^+]^2}$$
$$= 0.46 - \frac{0.0591}{2}\log\frac{0.025}{[0.005]^2}$$
$$= 0.46 - 0.0885 = 0.3715\ V$$

172. A 0.06 molar CH_3COOH solution offers a resistance of 55 ohms to a conductivity cell at 25° C. If the cell constant is 0.45 cm^{-1} and the molar conductance of CH_3COOH at infinite dilution is 398.5 ohm^{-1} cm^2 mol^{-1}.

ISC Specimen 2023

Calculate :

(a) Specific conductance

(b) Molar conductance

(c) Degree of dissociation

Ans :

(a) Specific conductance is given by

$$R = \rho\frac{l}{a} \qquad ...(i)$$

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Where, R = resistance, ρ = specific resistivity

and $\frac{l}{a}$ = cell constant

By putting these value in Eq. (i) we get,

$$55 = \rho \times 0.45$$

$$\rho = \frac{55}{0.45} = 122.2 \text{ ohm cm}$$

Specific conductance

$$(\kappa) = \frac{1}{\rho} = \frac{1}{122.2}$$

$$= 0.0082 \text{ ohm}^{-1}\text{cm}^{-1}$$

(b) $$\lambda_m = \kappa \times \frac{1000}{M}$$

$$= \frac{0.0082 \times 1000}{0.06} = 136.66 \text{ cm}^2\text{mol}^{-1}$$

(c) Degree of dissociation $(\alpha) = \frac{\Lambda_m}{\Lambda^o}$

Λ_m = molar conductivity

Λ° = molar conductivity at infinite dilution

$$\alpha = \frac{1350}{398.5} = 3.38$$

173. A current of 4 A is passed through a molten solution for 45 min 2.977 g of metal is deposited. Calculate the charge carried by the metal cation if its atomic mass is 106.4 g/mol.

ISC 2002

Ans :

Given, current $i = 4 \text{ A}$,

time, $t = 45 \text{ min} = 45 \times 60 \text{ s}$

weight of metal, $w = 2.977 \text{ g}$

$$2.977 = \frac{E \times 4 \times 45 \times 60}{96500}$$

(where, E is equivalent weight of metal)

$$E = \frac{96500 \times 2.977}{4 \times 45 \times 60}$$

$$= 26.6 \text{ g of metal}$$

Equivalent weight of the metal = 26.60 g

$$\text{Equivalent weight} = \frac{\text{Atomic weight}}{\text{Valency}}$$

$$\text{Valency} = \frac{106.4}{26.6} = 4$$

Hence, valency of the element = 4.

The metal cation can be M^{4+}

The charge of an electron is 1.6×10^{-19} C.

$$M^{4+} + 4e^- \longrightarrow M$$

Charge of 4 electrons $= 1.6 \times 10^{-19} \times 4$

(As $Q = ne^-$ where, n is the number of electrons $= 6.4 \times 10^{-19}$ C)

174. A cell is constructed by dipping a zinc rod in 0.1 M zinc nitrate solution and a lead rod in a 0.2 M lead nitrate solution.

$E^o_{Pb^{2+}/Pb} = -0.13$ V and $E^o_{Zn^{2+}/Zn} = -0.76$ V

(i) Write the spontaneous cell reaction.

(ii) Calculate standard emf and emf of the cell.

ISC 2004

Ans :

(i) Since, $E^o_{Pb^{2+}/Pb} > E^o_{Zn^{2+}/Zn}$

Hence, Pb will reduce and zinc will oxidise, i.e. Pb^{2+} will move towards cathode and Zn towards anode.

At anode, $Zn \longrightarrow Zn^{2+} + 2e^-$; $E^\circ = -0.76$ V

At cathode, $Pb^{2+} + 2e^- \longrightarrow Pb$; $E^\circ = -0.13$ V

Cell reaction, $Zn + Pb^{2+} \longrightarrow Pb + Zn^{2+}$

Cell representation is

$$Zn\,|\,Zn^{2+}(0.1\text{ M})\,||\,Pb^{2+}(0.2\text{ M})\,|\,Pb$$

(ii) $$E^o_{cell} = E^o_{cathode} - E^o_{anode}$$

$$= E^o_{Pb^{2+}/Pb} - E^o_{Zn^{2+}/Zn}$$

$$= -0.13 - (-0.76) = -0.13 + 0.76$$

$$E^o_{cell} = +0.63 \text{ V}$$

$$E_{cell} = E^o_{cell} - \frac{0.059}{n}\log\frac{[\text{Product}]}{[\text{Reactant}]}$$

(Here, $n = 2$)

$$= 0.63 - \frac{0.059}{2}\log\frac{(0.1)}{(0.2)}$$

$$= 0.63 - 0.0295\log(0.5)$$

$$= 0.63 - 0.0295(-0.30)$$

$$= 0.63 + 8.85 \times 10^{-3}$$

$$E_{cell} = 0.6388 \text{ V}$$

175. Calculate the emf and ΔG for the given cell at 25° C

$Cr(s)\,|\,Cr^{3+}(0.1\text{ M})\,||\,Fe^{2+}(0.01\text{ M})\,|\,Fe(s)$

Given, $E^o_{Cr^{3+}/Cr} = -0.74$ V, $E^o_{Fe^{2+}/Fe} = -0.44$ V

(1 F = 96500 C, $R = 8.314$ JK^{-1}mol^{-1})

ISC 2024

Ans :

Given, $E^o_{Cr^{3+}/Cr} = -0.74$ V,

$E^o_{Fe^{2+}/Fe} = -0.44$ V

For the cell,

At cathode, $(Fe^{2+} + 2e^- \longrightarrow Fe) \times 3$

At anode, $(Cr \longrightarrow Cr^{3+} + 3e^-) \times 2$

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Hence, $n = 6$

According to Nernst equation,

$$E_{cell} = E^{o}_{cell} - \frac{0.0591}{n}\log_{10}\frac{[\text{Product}]}{[\text{Reactant}]}$$

$$= E^{o}_{cell} - \frac{0.0591}{6}\log\frac{[Cr^{3+}]^2}{[Fe^{2+}]^3}$$

$$E^{o}_{cell} = E_{cathode} - E_{anode}$$

$$= -0.44 - (-0.74) = 0.30\ V$$

Given, $[Cr^{3+}] = 0.1\ M$ and $[Fe^{2+}] = 0.01\ M$

$$E_{cell} = 0.30 - \frac{0.0591}{6}\log\frac{[0.1]^2}{[0.1]^3} = 0.2902\ V$$

Also, we know that

$$\Delta G = -nFE_{cell}$$

$$= -6 \times 96500 \times 0.2902$$

$$= -168025.8\ J$$

$$= -168.03\ kJ$$

176. For the cell, $Zn\,|\,Zn^{2+}(\alpha = 1)\,||\,Cu^{2+}(\alpha = 1)\,|\,Cu$

Given that, $E^{o}_{Zn^{2+}/Zn} = -0.76\ V$, $E^{o}_{Cu^{2+}/Cu} = +0.339\ V$

(i) Write the cell reaction.

(ii) Calculate the emf and free energy change at 298 K involved in the cell.
(Faraday's constant equivalent^{-1})

ISC 2017, 2005

Ans :

(i) According to thermodynamics, free energy change (ΔG°) is equal to maximum work.

Hence, $-W_{max} = \Delta G^{\circ} = -nFE^{o}_{cell}$

At cathode,

$$Cu^{2+} + 2e^{-} \longrightarrow Cu;$$

$$E^{\circ} = 0.339\ V$$

At anode,

$$Zn \longrightarrow Zn^{2+} + 2e^{-};$$

$$E^{\circ} = 0.761\ V$$

Cell reaction,

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Cu(s) + Zn^{2+}(aq)$$

(ii) $E^{o}_{cell} = E^{o}_{cathode} - E^{o}_{anode}$

Given, $E^{o}_{Zn^{2+}/Zn} = -0.761\ V$

$E_{Cu^{2+},Cu} = +0.339\ V$

or $E^{o}_{Zn/Zn^{2+}} = 0.761\ V$

Hence, $E^{o}_{cell} = E^{o}_{Cu^{2+}/Cu} - E^{o}_{Zn^{2+}/Zn}$

$$= 0.339 - (-0.761) = 1.1\ V$$

Putting the value of E^{o}_{cell} in $\Delta G^{\circ} = -nFE^{o}_{cell}$

Where, $n = 2,\ F = 96500\ C$

$$\Delta G^{\circ} = -2 \times 96500 \times 1.1$$

$$= -212300\ J$$

$$= -212.3\ kJ$$

177. A current of 10 A is passed for 80 min and 27 s through a cell containing dilute sulphuric acid.

(i) How many moles of oxygen gas will be liberated at the anode?

(ii) Calculate the amount of zinc deposited at the cathode when another cell containing $ZnSO_4$ solution is connected in series (Zn = 65).

ISC 2007

Ans :

(i) Given, current $i = 10\ A$

$$t = 80\ \text{min}\ 27\ s$$

$$= 80 \times 60 + 27\ s = 4827\ s$$

Equivalent weight, E for oxygen $= 8$

Weight of O_2 liberated

$$= \frac{8 \times 10 \times 4827}{96500} = 4\ g$$

$$\text{Moles of oxygen} = \frac{\text{Weight}}{\text{Molecular weight}}$$

(Molecular weight of $O_2 = 16 \times 2 = 32$)

$$= \frac{4}{32} = 0.125\ \text{moles of}\ O_2$$

(ii) According to Faraday's second law of electrolysis When the same quantity of electricity is passed through the solutions of different electrolytes connected in series, the masses of the substances liberated (or deposited) at the electrodes are directly proportional to their equivalent masses.

$$\frac{\text{Mass of}\ O_2}{\text{Mass of Zn}} = \frac{\text{Equivalent weight of}\ O_2}{\text{Equivalent weight of Zn}}$$

Let x be the amount of Zn deposited

$$\frac{4}{x} = \frac{8}{\frac{65}{2}}\ (\text{equivalent weight of Zn} = \tfrac{65}{2})$$

$$x = 4 \times \frac{65}{2 \times 8} = 16.25\ g$$

178. The specific conductivity of a solution containing 5 g of anhydrous $BaCl_2$ (molecular weight = 208) in 1000 cm^3 of a solution is found to be 0.0058 $ohm^{-1}cm^{-1}$

Calculate the molar and equivalent conductivity of the solution.

ISC 2018

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Ans :

Specific conductivity

$$(\kappa) = 0.0058\ \text{ohm}^{-1}\text{cm}^{-1}$$

Molar mass of $BaCl_2 = 208\ \text{g mol}^{-1}$

As 5 g of $BaCl_2$ is present in $1000\ \text{cm}^3$ of the solution.

Molar concentration

$$(C) = \frac{1}{208} \times \frac{5}{1000} \times 1000$$
$$= 0.0240\ \text{mol L}^{-1}$$
$$= 241.67\ \text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$$

In $BaCl_2$, equivalent weight

$$= \frac{\text{molecular weight}}{2} = \frac{208}{2} = 104$$

Concentration of solution in gram equivalent per litre

$$= \frac{1}{104} \times \frac{1}{200} \times 1000 = 0.0480$$

Equivalent conductivity,

$$\Lambda_{eq} = \frac{\kappa \times 1000}{N}$$
$$= \frac{0.0058\ \text{ohm}^{-1}\text{cm}^{-1} \times 1000\ \text{cm}^3\text{L}^{-1}}{0.0480\ \text{g eqL}^{-1}}$$
$$= 120.83\ \text{ohm}^{-1}\text{cm}^2\text{eq}^{-1}$$

179. For the cell,

$\text{Cu} \mid \text{Cu}^{2+}(0.13\ \text{M}) \mid\mid \text{Ag}^{+}(0.01\ \text{M}) \mid \text{Ag}$

(i) Calculate the reduction potential of each electrode if the standard reduction potential for copper and silver electrodes are 0.34 V and 0.80 V respectively.

(ii) Calculate the emf of the cell.

(iii) Write the cell reaction.

(iv) Is this cell reaction spontaneous? Why?

ISC 2001

Ans :

(i) Reduction potential of $Ag^+ > Cu^2$. Hence, Ag^+ will get reduced and Cu will get oxidised.

Hence, Ag^+ will move towards cathode and Cu towards anode.

At anode, $\text{Cu} \longrightarrow \text{Cu}^{2+} + 2e^-$, $E^\circ = 0.39\ \text{V}$

At cathode, $(\text{Ag}^+ + e^- \longrightarrow \text{Ag}) \times 2$ $E^\circ = 0.80\ \text{V}$

Given, $[\text{Ag}^+] = 0.01\ \text{M}$, $E^\circ_{\text{Ag}^+/\text{Ag}} = 0.8\ \text{V}$

Reduction potential at cathode

$$E_{\text{Ag}^+/\text{Ag}} = E^\circ_{\text{Ag}^+/\text{Ag}} + \frac{0.0591}{1}\log[\text{Ag}^+]$$
$$= 0.8 + \frac{0.0591}{1}\log(0.01)$$
$$= 0.8 - 0.0591 \times 2$$
$$= 0.8 - 0.1182$$
$$= 0.6818\ \text{V}$$

Reduction potential at anode

$$E_{\text{Cu}^{2+}/\text{Cu}} = E^\circ_{\text{Cu}^{2+}/\text{Cu}} + \frac{0.0591}{2}\log[\text{Cu}^{2+}]$$
$$([\text{Cu}^{2+}] = 0.13\ \text{M})$$
$$= 0.39 + \frac{0.0591}{2}\log(0.13\ \text{V})$$
$$= 0.3638\ \text{V} (E^\circ_{\text{Cu}^{2+}/\text{Cu}} = 0.39\ \text{V})$$

(ii) $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$

$$= 0.6818 - 0.3638$$

$$E^\circ_{\text{cell}} = 0.3180\ \text{V}$$

(iii) Cell reaction

$$\text{At cathode, } 2\text{Ag}^+ + 2e^- \longrightarrow 2\text{Ag}$$
$$\text{At anode, } \text{Cu} \longrightarrow \text{Cu}^{2+} + 2e^-$$
$$\text{Cu} + 2\text{Ag}^+ \longrightarrow \text{Cu}^{2+} + 2\text{Ag}$$

(iv) For a reaction to be spontaneous, ΔG should be negative. For this cell, E_{cell} is positive and $\Delta G = -nFE^\circ$. Hence, this cell reaction is spontaneous.

180. A 0.05 M NH_4OH solution offers the resistance of 50 Ωto a conductivity cell at 298 K. If the cell constant is $0.50\ \text{cm}^{-1}$ and molar conductance of NH_4OH at infinite dilution is $471.4\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$. Calculate

(i) Specific conductance

(ii) Molar conductance

(iii) Degree of dissociation

ISC 2016

Ans :

Given $R = 50\ \Omega$,

Concentration = 0.05 M

Cell constant, $G^* = 0.50\ \text{cm}^{-1}$,

Molar conductance at infinite dilution,

$$\Lambda^\circ = 471.4\ \Omega^{-1}\text{cm}^2\text{mol}^{-1}$$

(i) Specific conductance $= G^*/R$

$$\kappa = \frac{0.5}{50} = 0.01\ \Omega^{-1}\text{cm}^{-1}$$

(ii) Molar conductance,

$$\Lambda_m = \frac{1000 \times \kappa}{\text{molarity}}$$
$$= \frac{1000 \times 0.01\ \Omega^{-1}\text{cm}^{-1}}{0.05\ \text{mol cm}^{-3}}$$
$$= 200\ \Omega^{-1}\text{cm}^2\text{mol}^{-1}$$

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(iii) Degree of dissociation

$$(\alpha) = \frac{\Lambda_m}{\Lambda_m^o}$$

$$= \frac{200\ W^{-1}cm^2mol^{-1}}{471.4\ W^{-1}cm^2mol^{-1}} = 0.42$$

181. For the following cell, calculate the emf.

$Al\,|\,Al^{3+}(0.01\,M)\,||\,Fe^{2+}(0.02\,M)\,|\,Fe$

Given : $E^o_{Al^{3+}/Al} = -1.66\,V$, $E^o_{Fe^{2+}/Fe} = -0.44\,V$

ISC 2009

Ans :

Given, $E^o_{Al^{3+}/Al} = -1.66\,V$, $E^o_{Fe^{2+}/Fe} = -0.44\,V$

For the cell,

At cathode, $(Fe^{2+} + 2e^- \longrightarrow Fe) \times 3$; $E^\circ = -0.44\,V$

At anode, $(Al \longrightarrow Al^{3+} + 3e^-) \times 2$; $E^\circ = -1.66\,V$

Hence, $n = 6$

According to Nernst equation,

$$E_{cell} = E^o_{cell} - \frac{0.0591}{n}\log_{10}\frac{[Product]}{[Reactant]}$$

$$= E^o_{cell} - \frac{0.0591}{6}\log\frac{[Al^{3+}]^2}{[Fe^{2+}]^3}$$

$$E^o_{cell} = E^o_{cathode} - E^o_{anode}$$

$$= -0.44 - (-1.66)$$

$$= -0.44 + 1.66 = 1.22$$

Given, $[Al^{3+}] = 0.01\,M$, $[Fe^{2+}] = 0.02\,M$

$$E_{cell} = 1.22 - \frac{0.0591}{6}\log\frac{(0.01)^2}{(0.02)^3}$$

$$= 1.22 - 9.85 \times 10^{-3}\log(12.5)$$

$$= 1.22 - 9.85 \times 10^{-3} \times 1.097$$

$$= 1.22 - 0.012 = 1.208\,V$$

182. The specific conductance of a 0.01 M solution of acetic acid at 298 K is $1.65 \times 10^{-4}\,\Omega^{-1}\,cm^{-1}$.

The molar conductance at infinite dilution for H^+ ion and CH_3COO^- ion are $349.1\,\Omega^{-1}\,cm^2\,mol^{-1}$ and $40.9\,\Omega^{-1}\,cm^2\,mol^{-1}$ respectively, calculate :

(i) molar conductance of the solution.

(ii) degree of dissociation of CH_3COOH.

(iii) dissociation constant for acetic acid.

Ans :

(i) Specific conductance $= 1.65 \times 10^{-4}\,\Omega^{-1}cm^{-1}$

Concentration $= 0.01$ M

Limiting molar conductivity,

$$\Lambda^o_{CH_3COOH} = (349.1 + 40.9)\,\Omega^{-1}cm^2mol^{-1}$$

$$= 390\,\Omega^{-1}cm^2mol^{-1}$$

$$\Lambda_m = \frac{\kappa \times 1000}{C}$$

$$= \frac{1.65 \times 10^{-4}\,\Omega^{-1}cm^{-1} \times 1000}{0.01}$$

$$= 16.5\,\Omega^{-1}cm^2mol^{-1}$$

(ii) Degree of dissociation,

$$\alpha = \frac{\text{Molar conductance of substance}}{\text{Molar conductance at infiinte dilution}}$$

$$\alpha = \frac{16.5}{390} = 0.042$$

(iii) Dissociation constant for acetic acid

$$K = \frac{C\alpha^2}{1-\alpha} = \frac{0.01 \times (0.042)^2}{1 - 0.042}$$

$$K = 1.8 \times 10^{-5}\,mol/L$$

183. (i) The resistance of a conductivity cell with 0.1 M KCl solution is 200 ohm. When the same cell is filled with 0.02 M NaCl solution, the resistance is 1100 ohm. If the conductivity of 0.1 M KCl solution is $0.0129\,ohm^{-1}\,cm^{-1}$, calculate the cell constant and molar conductivity of 0.02 M NaCl solution.

(ii) The emf (E^o_{cell}) of the following reaction is 0.89 V.

$$3Sn^{4+} + 2Cr \longrightarrow 3Sn^{2+} + 2Cr^{3+}$$

Calculate the value of ΔG° for the reaction. Predict whether the above reaction will be spontaneous or not.

ISC 2018

Ans :

(i) For 0.1 M KCl solution, $R = 200\,\Omega$

$$\kappa_{KCl} = 0.0129\,\Omega^{-1}cm^{-1}$$

$$\kappa_{KCl} = \frac{G^*}{R} \qquad (G^* = \text{cell constant})$$

$$0.0129 = \frac{G^*}{200}$$

$$G^* = 200 \times 0.0129 = 2.58\,cm^{-1}$$

Cell is same, so $\kappa_{KCl} = \kappa_{NaCl}$

For 0.02 M NaCl solution,

$$\lambda_m = \frac{\kappa_{NaCl} \times 1000}{C}$$

$$= \frac{0.0129 \times 1000}{0.02} = 645\,\Omega^{-1}cm^2mol^{-1}$$

(ii) At cathode, $(Sn^{4+} + 2e^- \longrightarrow Sn^{2+}) \times 3$

At anode, $\underline{(Cr \longrightarrow Cr^{3+} + 3e^-) \times 2}$

$3Sn^{4+} + 3Cr + 6e^- \longrightarrow 3Sn^{2+} + 2Cr^{3+} + 6e^-$

So, $n = 6$

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Given, $E^{\circ}_{cell} = 0.89\ V$

By the equation, $\Delta G^{\circ} = -nFE^{\circ}_{cell}$

$= -6 \times 96500 \times 0.89$

$= -515.3\ kJ$

ΔG° is –ve so the reaction will be spontaneous.

184. Resistance of a conductivity cell filled with $0.1\ mol\ L^{-1}$ KCl solution is $100\ \Omega$. If the resistance of the same cell when filled with $0.02\ mol\ L^{-1}$ KCl solution is $520\ \Omega$, Calculate the conductivity and molar conductivity of $0.02\ mol\ L^{-1}$ KCl solution. The conductivity of $0.1\ mol\ L^{-1}$ KCl solution is $1.29 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$.

ISC Specimen 2018

Ans :

For electrolyte having 0.01 mol L^{-1} KCl solution,

Molarity $= 0.1\ mol L^{-1}$

Resistance $= 100\ \Omega$

Conductivity $= 1.29 \times 10^{-2}\ \Omega^{-1} cm^{-1}$

Cell constant (G^*)

$=$ Resistance $(R) \times$ Conductivity (κ)

$= 100\ \Omega \times 1.29 \times 10^{-2}\ \Omega^{-1} cm^{-1}$

$= 1.29\ cm^{-1}$

For electrolyte having 0.01 mol L^{-1} KCl solution,

Molarity $= 0.02\ mol\ L^{-1}$

Resistance $= 520\ \Omega$

Conductivity of 0.02 mol L^{-1} KCl solution,

$$\kappa = \frac{\text{Cell constant}}{\text{Resistance}}$$

$$= \frac{1.29\ (cm^{-1})}{520\ (\Omega)}$$

$$= 2.481 \times 10^{-3}\ cm^{-1}\Omega^{-1}$$

Molar conductivity,

$$\Lambda_m = \frac{\kappa \times 1000}{\text{Molarity}}$$

$$= \frac{2.481 \times 10^{-3} \times 1000}{0.02}$$

$$= 124\ \Omega^{-1} cm^2 mol^{-1}$$

185. Consider the reaction, $2Ag^+ + Cd \longrightarrow 2Ag + Cd^{2+}$

The standard reduction of Ag^+/Ag and Cd^{2+}/Cd are $+0.80$ V and -0.40 V respectively.

(i) Give the cell representation.

(ii) What is the standard cell emf, E° ?

(iii) What will be the emf of the cell if concentration of Cd^{2+} is 0.1 M and Ag^+ is 0.2 M ?

(iv) Will the cell work spontaneously for the condition shown in (iii) above?

ISC 2016, 2011

Ans :

(i) Given reaction is

$$2Ag^+ + Cd \longrightarrow 2Ag + Cd^{2+}$$

Reduction potential of $\underset{(0.80)}{Ag^+/Ag} > \underset{(-0.40)}{Cd^{2+}/Cd}$

Hence, Ag^+ will move towards cathode and Cd towards anode.

At cathode, $(Ag^+ + e^- \longrightarrow Ag) \times 2$, $E^{\circ} = 0.80$ V

At anode, $Cd \longrightarrow Cd^{2+} + 2e^-$, $E^{\circ} = +0.40$ V

Hence, cell representation is

$$Cd\,|\,Cd^{2+}\,||\,Ag^+/Ag$$

(ii) Given, $E^{\circ}_{Ag^+/Ag} = +0.80$ V

and $E^{\circ}_{Cd^{2+}/Cd} = -0.40$ V

Standard cell emf,

$$E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode}$$

$$= 0.80 - (-0.40)$$

$$= 0.80 + 0.40$$

$$= 1.20\ V$$

(iii) Given, $[Cd^{2+}] = 0.1$ M and $[Ag^+] = 0.2$ M

According to Nernst equation,

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{n} \log \frac{[\text{Product}]}{[\text{Reactant}]}$$

$$= E^{\circ}_{cell} - \frac{0.0591}{n} \log \frac{[Cd^{2+}]}{[Ag^+]^2}$$

Here, $n = 2$

Hence, $E_{cell} = 1.20 - \frac{0.059}{2} \log \frac{(0.1)}{(0.2)^2}$

$$= 1.20 - \frac{0.059}{2}[\log 10 - 2 \log 2]$$

$$= 1.20 - \frac{0.059}{2} \times 0.398$$

$$= 1.20 - 0.01 = 1.19\ V$$

(iv) For a reaction to be spontaneous, ΔG should be negative, i.e.

$$\Delta G = -nFE^{\circ}_{cell}$$

As $E^{\circ}_{cell} = 1.19$ V, which is positive, hence, ΔG is negative. Thus, the reaction would be spontaneous.

NODIA

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CHAPTER 3

CHEMICAL KINETICS

SUMMARY

1. CHEMICAL KINETICS

It is the branch of chemistry that deals with the study of the speed or rate of chemical reactions, the factors that influence these rates, and the mechanisms through which the reactions occur.

2. RATE OF REACTION

It is change in concentration of a reactant or product per unit time.

(a) Average rate of reaction : It is defined as the rate of reaction measured over a long period of time.

Let a reaction $aA + bB \longrightarrow cC + dD$

$$\text{Average rate of reaction} = \frac{-1}{a}\frac{\Delta[A]}{\Delta t} = \frac{-1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$$

(b) Instantaneous rate of reaction : It is defined as the average rate of reaction when it is measured over a very small interval of time.

Let a reaction $aA + bB \longrightarrow cC + dD$

Instantaneous rate of reaction

$$r = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}$$

It may be noted that negative sign before the expression of a reactant indicates that its conc. decreases with the passage of time. Units of rate of reaction are mol L^{-1} time^{-1} or atm time^{-1}

3. FACTORS AFFECTING THE RATE OF REACTION

Following factors are affecting that rate of reaction :

(a) Conc. of reactants :

Rate of reaction $\propto$ Conc. of reactants.

(b) Temperature of the system :

Rate of reaction $\propto$ Temperature

(c) Nature of reactants and products

Rate of reaction

$$\propto \frac{1}{\text{Bond dissociation energies of reactants}}$$

(d) Presence of catalyst

The rate of a reaction increases in the presence of a catalyst.

(e) Surface area

Rate of reaction $\propto$ Surface area of reactants.

(f) Exposure to radiation

The rate of a reaction is increased by the use of certain radiations.

4. RATE LAW

The mathematical expression which denotes the experimentally observed rate of a reaction in terms of the concentration of the reactants which actually influence the rate of reaction is called rate law.

Let a reaction $aA + bB \longrightarrow$ Products

So, Rate of reaction $= k[A]^{\alpha}[B]^{\beta}$

α and β are the powers of concentration of reactants which actually influence the rate of the reaction.

Where k = rate constant and $\alpha \leq a$, $\beta \leq b$.

5. ORDER OF THE REACTION

It is defined as the sum of the powers to which the concentration terms of the reactants are raised in the rate law equation of a chemical reaction.

$$\text{Order of reaction} = \alpha + \beta$$

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6. RATE CONSTANT AND ITS UNIT

It is defined as the rate of reaction, when the concentration of each of the reactants is unity. In general, the units of rate constant for the reaction of nth order are:

$$\text{Units of } k = \text{mol}^{1-n}\text{L}^{n-1}\text{time}^{-1}$$

For the gaseous reaction.

$$\text{Units of } k = \text{atm}^{1-n}\text{time}^{-1}$$

7. MOLECULARITY

Molecularity of a simple reaction is defined as the total number of molecules of reactants which collide simultaneously to bring a chemical reaction.

Let a reaction $a\text{A} + b\text{B} \longrightarrow$ Products

So, Molecularity $= a + b$

8. INTEGRATED RATE EXPRESSION

The integrated rate expression for different reaction are as follows:

(a) For a zero order reaction :

$$k = \frac{[A]_0 - [A]}{t} = \frac{x}{t}$$

Where $[A]_0 =$ initial conc. of reactant

$[A] =$ conc. of reactant after t time

and $[A]_0 = a$,

and $[A] = a - x$

Note : If $[A] = \frac{[A_0]}{2}$, then

$$k = \frac{[A]_0 - \frac{[A]_0}{2}}{t_{½}}$$

So, $$t_{½} = \frac{[A]_0}{2k}$$

Where $t_{½} =$ half-life time

(b) For a first order reaction

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]_t}$$

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

Where $a =$ initial conc. of $[A]_0$ $(a - x)$

$[A]_t$ conc. after time t.

When half reaction is completed, then

$$k = \frac{2.303}{t_{½}} \log \frac{[A]}{\frac{[A]_0}{2}}$$

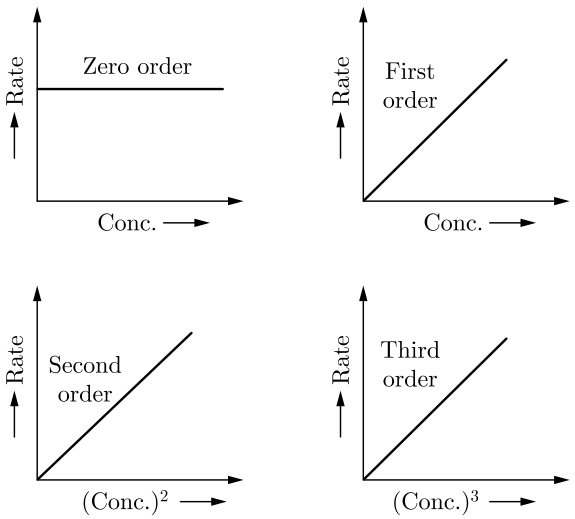
$$k = \frac{0.693}{t_{½}}$$

$$t_{½} = \frac{0.693}{k}$$

In general, $$t_{½} \propto \frac{1}{[A]_0^{n-1}}$$

9. EXPERIMENTAL DETERMINATION OF ORDER OF REACTION

(a) **Graphical method :** This method is used when there is only one reactant. In this method, a graph is plotted between rate of reaction and concentration.



(b) **Integrated rate expression method :** In this method, the kinetic data (obtained from experiment) is fitted to different integrated rate equations, whenever the data fits with the equation for the correct order of the reaction, it will give constant value of rate constant.

(c) **Initial rate method :** This method is used to calculate the order of those reactions, which contain more than one reactants and order may be zero, whole number or a fraction.

(d) **Ostwald's isolation method :** This method is used to find the order of a reaction with respect to one reactant at a time. The total order of the reaction is then equal to the sum of the orders of reaction for individual reactants.

(e) **Half-life period method :** In this method, the graphs are plotted between $t_{½}$ and $[A]_0$.

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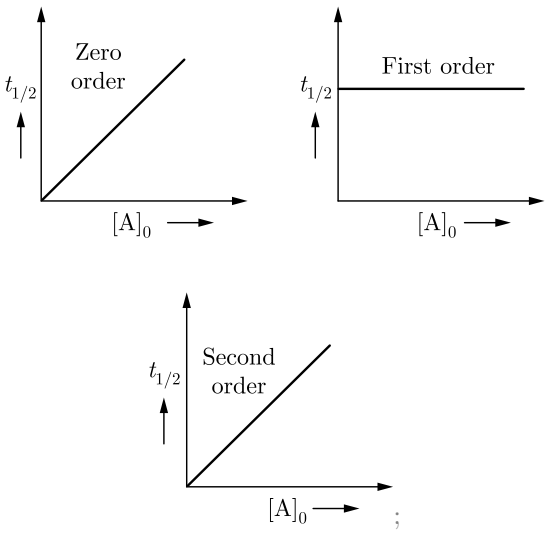
These graphs are given below:



10. PSEUDO CHEMICAL REACTIONS

Those reactions which appear to be of higher order but actually follow lower order kinetics are called Pseudo chemical reactions.

Example :

Following reactions follows first order kinetics.

$$\underset{\text{Sugar}}{C_{12}H_{12}O_{11}} + \underset{\text{(Excess)}}{H_2O} \xrightarrow[\Delta]{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

For this reaction, Rate $\propto [C_{12}H_{22}O_{11}]$

It is because water is present in such a large excess that its conc. remains almost constant during the reaction.

11. COLLISION THEORY OF REACTION RATES

According to collision theory, the rate of a reaction depends upon the collision frequency (z) and the fraction of effective collisions (f). So,

$$\text{Rate of reaction} \propto z \times f$$

(a) With the increase in temperature, the kinetic energy of molecules increases and this leads to an increase in collision frequency (z), as the average kinetic energy of the molecules is directly proportional to absolute temperature.

(b) For effective collision, the colliding molecules must have more than or equal to certain minimum amount of energy called threshold energy (E°) and proper orientation.
On increasing the temperature, the fraction of effective collisions (f) increases due to which rate of reaction increases.

12. ARRHENIUS EQUATION

This equation gives us the variation of rate constant of a reaction with temperature. This equation gives a relationship between rate constant (k) and temperature (T) as

$$k = Ae^{-E_a/RT}$$

Where, A = frequency factor

E_a = activation energy

T = absolute temperature

R = Gas constant

Talking logarithm, we have

$$\log k = \log A - \frac{E_a}{2.303\,RT}$$

13. CALCULATION OF ACTIVATION ENERGY, E_a

Activation energy can be determined by measuring the values of rate constant at two different temperatures. Let k_1 and k_2 are the rate constants for the reaction at temperatures T_1 and T_2 respectively, then

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

14. AMOUNT OF SUBSTANCE

Amount of substance left after n half lines

$$= \frac{[A]_0}{2^n}$$

15. RATE CONSTANT (K)

(a) For reaction $N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2}O_2$

$$k = \frac{2.303}{t} \log \frac{V_\infty}{V_\infty - V_t}$$

Where V_t = Volume of O_2 after time t

V_∞ = Volume of O_2 after infinite time

(b) For reaction $NH_4NO_2(aq) \longrightarrow 2H_2O + N_2$
Same expression as above is used and volume of N_2 is taken into account.

(c) For reaction $H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2$

$$k = \frac{2.303}{t} \log \frac{V_0}{V_t}$$

Where V_0 = Volume of $KMnO_4$ used for titration at $t = 0$,

V_t = Volume of $KMnO_4$ used for titration after time t.

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(d) For reaction

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

$$k = \frac{2.303}{t} \log \frac{V_\infty - V_0}{V_\infty - V_t}$$

Where V_0, V_t, V_∞ are volumes of NaOH used for titration of same volume of reaction mixture after 0, t and ∞ time.

(e) For reaction

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$k = \frac{2.303}{t} \log \frac{r_0 - r_\infty}{r_0 - r_t}$$

Where r_0, r_t and r_∞ are polarimetric readings after time 0, t and ∞ respectively.

(f) In the Arrhenius equation, when $T \to \infty$, then $k = A.\ e^\circ = n$ and rate becomes independent of temperature. Further in a reaction,

when $E_a = 0$, then $k = A$

i.e., Every collision of reactant molecules is effective, Thus, activation energy of a reaction cannot be zero.

OBJECTIVE QUESTIONS

1. In a plot of $\log k$ vs $1/T$, the slope is

ISC 2012

(a) $-E_a/2.303$ (b) $E_a/2.303R$

(c) $E_a/2.303$ (d) $-E_a/2.303R$

Ans : (d) $-E_a/2.303R$

In the plot of $\log k$ vs $1/T$ the slope is $-E_a/2303R$

2. For a first order reaction the rate constant for the decomposition of N_2O_5 is $6 \times 10^{-4}\ s^{-1}$. The half-life period for the decomposition (in seconds) is

ISC 2015

(a) 11.55 (b) 115.5

(c) 1155 (d) 1.155

Ans : (c) 1155

Rate constant for first order reaction of N_2O_5

$$\text{Decomposition} = 6 \times 10^{-4}\ s^{-1}$$

From half-life equation of first order reaction.

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{6 \times 10^{-4}}$$

$$t_{1/2} = 1155$$

3. A student observed that powdered calcium carbonate reacts much faster with dilute hydrochloric acid than marble chips of the same mass. Which factor is mainly responsible for the increased rate of reaction?

ISC 2024

(a) Increase in activation energy

(b) Increase in surface area

(c) Decrease in concentration

(d) Change in order of reaction

Ans : (b) Increase in surface area

Powdered calcium carbonate provides a much larger surface area than marble chips. Greater surface area exposes more reactant particles for collision with acid molecules. As collision frequency increases, the number of effective collisions also increases, thereby increasing the overall rate of the chemical reaction significantly.

4. The Arrhenius equation explains the relationship between:

ISC 2008

(a) Concentration and time

(b) Pressure and volume

(c) Rate constant and temperature

(d) Molecularity and activation energy

Ans : (c) Rate constant and temperature

Arrhenius equation describes how rate constant changes with temperature and activation energy. As temperature increases, rate constant generally increases exponentially because more molecules acquire sufficient energy to overcome the activation energy barrier and react effectively.

5. A chemical reaction was found to proceed at the same rate even after changing the concentration of reactant. The reaction is most likely:

ISC 2005

(a) First order

(b) Second order

(c) Zero order

(d) Third order

Ans : (c) Zero order

In zero order reactions, the reaction rate remains constant and does not depend upon concentration of reactants. Even if concentration changes during the reaction, the rate remains unchanged because the reacting surface or catalyst becomes saturated and limits the reaction rate.

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6. A student plotted log concentration versus time for a reaction and obtained a straight line with negative slope. The reaction follows:

ISC 2024

(a) Zero order kinetics

(b) First order kinetics

(c) Second order kinetics

(d) Fractional order kinetics

Ans : (b) First order kinetics

First order reactions show exponential decrease in concentration with time. Therefore a graph between log concentration and time gives a straight line with negative slope equal to $-k/2.303$. This graphical method is commonly used to experimentally identify first order reactions.

7. In a first order reaction, the half-life period remains constant because it is independent of:

ISC 2018

(a) Rate constant

(b) Temperature

(c) Initial concentration

(d) Activation energy

Ans : (c) Initial concentration

For first order reactions, half-life depends only upon the rate constant and not on initial concentration of reactant. Therefore the time required for concentration to become half remains constant throughout the reaction, irrespective of how much reactant is initially present.

8. A reaction has the rate law:

Rate $= k[A]^2[B]$

The overall order of the reaction is:

ISC 2009

(a) 1

(b) 2

(c) 3

(d) 4

Ans : (c) 3

The overall order of a reaction is obtained by adding the powers of concentration terms present in the rate law expression. Here, the powers are 2 and 1 respectively. Therefore total order becomes 3, indicating the reaction is third order overall.

9. Increase in temperature generally increases the rate of reaction because:

ISC 2011, 2004

(a) Activation energy becomes zero

(b) Number of effective collisions increases

(c) Molecularity increases

(d) Equilibrium constant becomes negative

Ans : (b) Number of effective collisions increases

Increase in temperature raises the kinetic energy of reactant molecules. As a result, molecules collide more frequently and with greater energy. Consequently, a larger fraction of collisions possess energy equal to or greater than activation energy, thereby increasing reaction rate significantly.

10. A reaction having high activation energy usually proceeds slowly because:

ISC 2020

(a) Rate constant becomes zero

(b) Very few molecules possess sufficient energy

(c) Molecularity becomes fractional

(d) Concentration remains constant

NODIA

Ans : (b) Very few molecules possess sufficient energy

Activation energy represents the minimum energy required for effective collision. When activation energy is very high, only a small fraction of molecules possess enough kinetic energy to react successfully. Therefore the number of effective collisions decreases and the reaction becomes slow.

11. In collision theory, effective collisions are collisions which:

ISC 2024

(a) Occur at low temperature

(b) Have proper orientation and sufficient energy

(c) Involve catalysts only

(d) Produce heat immediately

Ans : (b) Have proper orientation and sufficient energy

According to collision theory, not all collisions result in product formation. Molecules must collide with energy greater than or equal to threshold energy and also possess proper orientation. Only such effective collisions successfully lead to chemical reaction and product formation.

12. Which statement is correct regarding molecularity?
ISC 2010

(a) It can be fractional

(b) It may be zero

(c) It is always a whole number

(d) It changes with temperature

Ans : (c) It is always a whole number

Molecularity represents the number of reactant molecules colliding simultaneously in an elementary reaction step. Since actual molecules are involved, molecularity must always be a positive whole number and can never be fractional or zero.

13. A catalyst increases the rate of both forward and backward reactions because it:
ISC 2009

(a) Changes equilibrium constant

(b) Alters enthalpy change

(c) Lowers activation energy for both reactions

(d) Increases molecularity

Ans : (c) Lowers activation energy for both reactions

Catalysts provide alternative reaction pathways of lower activation energy for both forward and reverse reactions. Hence both reactions become faster equally. However, the catalyst does not alter equilibrium constant, enthalpy change or final equilibrium composition of the reaction system.

14. The unit of rate constant for a first order reaction is:
ISC 2013

(a) mol L^{-1} s^{-1}

(b) s^{-1}

(c) L mol^{-1} s^{-1}

(d) mol^2 L^{-2} s^{-1}

Ans : (b) s^{-1}

For first order reactions, rate depends linearly upon concentration of a single reactant. Therefore concentration units cancel while deriving the unit of rate constant, leaving only reciprocal time unit, represented as s^{-1}.

15. Hydrolysis of ester in presence of excess water is an example of:
ISC 2009

(a) Zero order reaction

(b) Second order reaction

(c) Pseudo first order reaction

(d) Third order reaction

Ans : (c) Pseudo first order reaction

In ester hydrolysis, water is present in very large excess and its concentration remains practically constant throughout the reaction. Therefore the rate appears to depend only upon concentration of ester, making the reaction behave like a first order reaction.

16. Which factor does not affect the value of rate constant of a reaction?
ISC 2025

(a) Temperature

(b) Catalyst

(c) Nature of reactants

(d) Initial concentration of reactants

Ans : (d) Initial concentration of reactants

Rate constant is characteristic of a reaction at a particular temperature and depends upon catalyst and nature of reactants. It does not depend upon initial concentration because concentration affects only reaction rate, not the intrinsic rate constant of the reaction.

17. A student carried out the decomposition of hydrogen peroxide in two separate flasks, one in presence of MnO_2 and the other without catalyst. The reaction in the first flask was much faster because MnO_2:
ISC 2002

(a) Increased concentration of hydrogen peroxide

(b) Lowered activation energy of the reaction

(c) Changed equilibrium constant of the reaction

(d) Increased threshold energy of molecules

Ans : (b) Lowered activation energy of the reaction

MnO_2 acts as a catalyst and provides an alternative pathway having lower activation energy. Due to lower activation energy, a larger number of molecules undergo effective collisions per unit time. Therefore decomposition of hydrogen peroxide becomes much faster in presence of the catalyst without altering the equilibrium constant.

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18. During an experiment, a student observed that doubling the concentration of reactant doubled the rate of reaction. The reaction is:

ISC 2023

(a) Zero order with respect to reactant

(b) First order with respect to reactant

(c) Second order with respect to reactant

(d) Third order with respect to reactant

Ans : (b) First order with respect to reactant

In first order reactions, rate is directly proportional to concentration of reactant. Therefore when concentration is doubled, the reaction rate also doubles. Such proportional dependence between concentration and rate is characteristic of first order kinetics.

19. A graph between concentration of reactant and time for a zero order reaction gives:

ISC 2004

(a) Straight line with positive slope

(b) Straight line with negative slope

(c) Exponential curve

(d) Horizontal straight line

Ans : (b) Straight line with negative slope

In zero order reactions, concentration decreases uniformly with time because the rate remains constant and independent of concentration. Therefore plotting concentration against time produces a straight line having negative slope equal to –k.

20. A reaction has high activation energy. Which condition will increase its rate most effectively?

ISC 2003

(a) Decreasing temperature

(b) Increasing concentration slightly

(c) Increasing temperature significantly

(d) Reducing surface area of reactants

Ans : (c) Increasing temperature significantly

Reactions having high activation energy are highly sensitive to temperature changes. Increase in temperature greatly increases the number of molecules possessing energy greater than activation energy, thereby increasing the number of effective collisions and accelerating the reaction considerably.

21. In a pseudo first order reaction, the concentration of one reactant is taken in large excess so that:

ISC 2024

(a) Molecularity becomes zero

(b) Its concentration remains practically constant

(c) Activation energy decreases completely

(d) Reaction becomes reversible

Ans : (b) Its concentration remains practically constant

In pseudo first order reactions, one reactant is present in very large excess compared to the other reactant. Therefore its concentration does not change appreciably during the reaction and effectively becomes constant, causing the reaction to behave kinetically as first order.

22. A chemistry student concluded that a reaction is first order because its half-life remained constant throughout the reaction. This conclusion is correct because:

ISC 2012, 2005

(a) Half-life of first order reactions depends only on rate constant

(b) Half-life increases with concentration

(c) Rate becomes independent of concentration

(d) Molecularity remains constant

Ans : (a) Half-life of first order reactions depends only on rate constant

In first order reactions, half-life is independent of initial concentration and depends only upon the rate constant. Therefore equal time intervals are required for concentration to reduce to half repeatedly throughout the course of the reaction.

23. During collision between reacting molecules, products are formed only when molecules:

ISC 2006

(a) Possess low kinetic energy

(b) Collide in random orientation only

(c) Possess sufficient energy and proper orientation

(d) Have equal molecular masses

Ans : (c) Possess sufficient energy and proper orientation

According to collision theory, only effective collisions result in chemical reaction. For a collision to become effective, reacting molecules must possess energy equal to or greater than threshold energy and must collide with proper orientation.

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24. A gaseous reaction was found to proceed faster at high pressure because:

ISC 2010

(a) Activation energy became zero

(b) Collision frequency increased

(c) Molecularity decreased

(d) Threshold energy increased

Ans : (b) Collision frequency increased

Increasing pressure decreases intermolecular distance between gaseous molecules. As molecules come closer, frequency of collisions increases significantly. Greater collision frequency increases the probability of effective collisions and therefore increases the reaction rate.

25. Which statement correctly distinguishes order from molecularity?

ISC 2025

(a) Both are always equal

(b) Order is experimental while molecularity is theoretical

(c) Molecularity may be fractional

(d) Order can never be zero

Ans : (b) Order is experimental while molecularity is theoretical

Order of reaction is determined experimentally from the rate law and may even be fractional or zero. Molecularity, however, represents the number of molecules colliding simultaneously in an elementary step and is always a whole number.

26. The rate constant of a reaction increased when temperature was raised from 298 K to 308 K. This happened because:

ISC 2002

(a) Number of reactant molecules increased

(b) Activation energy became negative

(c) Larger fraction of molecules acquired activation energy

(d) Molecularity of reaction increased

Ans : (c) Larger fraction of molecules acquired activation energy

Increase in temperature raises the average kinetic energy of molecules. Consequently, a greater fraction of molecules acquires energy equal to or greater than activation energy, increasing effective collisions and thereby increasing the value of the rate constant.

27. During decomposition of hydrogen peroxide, the reaction becomes much faster after adding MnO_2. The catalyst increases the reaction rate because it:

ISC 2010

(a) Increases threshold energy

(b) Provides an alternative pathway with lower activation energy

(c) Changes equilibrium constant

(d) Increases concentration of reactants

Ans : (b) Provides an alternative pathway with lower activation energy

Catalysts accelerate reactions by providing an alternative reaction pathway having lower activation energy. Because of reduced activation energy, a larger number of reactant molecules acquire sufficient energy for effective collisions. Therefore the reaction proceeds more rapidly without any permanent chemical change in the catalyst itself.

28. The reaction between X and Y is first order with respect to X and second order with respect to Y. If the concentration of X is halved and the concentration of Y is doubled, the rate of reaction will be

ISC 2008

(a) same as the initial value

(b) three times the initial value

(c) double the initial value

(d) half the initial value

Ans : (c) double the initial value

Given, $X + Y \longrightarrow$ Product

As the reaction is first order with respect to X and second order with respect to Y.

Hence, rate of reaction, $r_1 = k[X]^1[Y]^2$

If concentration of X is halved, i.e. $\frac{[X]}{2}$ and concentration of Y is doubled, i.e. $[2Y]$.

Then, new rate of reaction,

$$r_2 = k\left[\frac{X}{2}\right]^1[2Y]^2$$

$$= k \times 2[X][Y]^2$$

Hence, $r_2 = 2r_1$

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29. The half-life period of a first order reaction is 20 minutes. The time required for the concentration of the reactant to change from 0.16 M to 0.02 M is
ISC 2017

(a) 80 minutes (b) 60 minutes
(c) 40 minutes (d) 20 minutes

Ans : (b) 60 minutes

Given, $t_{1/2} = 20\,\text{min}$

$[A]_0$ = initial concentration = 0.16 M

$[A]$ = concentration left after time 't' = 0.02 M

$$k = \frac{0.696}{t_{1/2}}$$

$$= \frac{0.693}{20} = 0.03465\,\text{min}^{-1}$$

For first order reaction,

$$\text{Rate constant } (k) = \frac{2.303}{t}\log\frac{[A]_0}{[A]}$$

$$t = \frac{2.303}{0.03465}\log\frac{[0.16]}{[0.02]}$$

$$= 60 \text{ minutes.}$$

30. 75% of a first order reaction was completed in 32 min. When was 50% of the reaction completed?
ISC 2011

(a) 24 min (b) 16 min
(c) 8 min (d) 4 min

Ans : (b) 16 min

Time $t_{75\%} = 32\,\text{min}$, suppose the initial concentration is $[A]_0$. Since, the reaction is 75% complete in 32 min, the concentration left after 32 min will be given by

$$[A] = [A_0] \times \frac{(100-75)}{100} = [A_0] \times \frac{1}{4}$$

Then from the formula,

$$k = \frac{2.303}{t}\log\frac{[A]_0}{[A]}$$

We get, $$k = \frac{2.303}{32}\log\frac{[A]_0}{[A]_0/4}$$

$$= \frac{2.303}{32} \times \log 4$$

For 50% completion,

$$t_{1/2} = \frac{0.693}{k}$$

$$t_{1/2} = \frac{0.693 \times 32}{2.303 \times \log 4}$$

Where, $[\log 4 = 0.602]$

$$= \frac{0.693 \times 32}{2.303 \times 0.602} = 15.99 \approx 16\,\text{min}$$

31. Suppose 50 bacteria are placed in a flask containing nutrients, so that they can multiply. A study at 35°C gave the following results :
ISC Specimen 2023

Time (in minutes)	0	15	30	45	60
Number of bacteria	100	200	400	800	1600

Answer the following questions.

(i) This multiplication of bacteria follows
(a) zero order reaction
(b) first order reaction
(c) second order reaction
(d) third order reaction

Ans : (b) first order reaction

In this data, as the time increases the growth of bacteria increases in the same order. So, it follows first order reaction.

(ii) The rate constant for the reaction is
(a) 0.0462 min^{-1} (b) 0.462 min^{-1}
(c) 4.62 min^{-1} (d) 46.2 min^{-1}

Ans : (a) 0.0462 min^{-1}

The rate constant of first order is given by

$$k = -\frac{2.303}{t}\log\frac{[A]}{[A_0]}$$

$$k = \frac{-2.303}{15}\log\frac{100}{200}$$

$$k = \frac{-2.303}{15} \times (-0.301)$$

$$k = 0.0462\,\text{min}^{-1}$$

(iii) The half-life period $(t_{1/2})$ of the reaction is
(a) 1500 minutes (b) 150 minutes
(c) 15 minutes (d) 1.5 minutes

Ans : (c) 15 minutes

Half-life of first order reaction is $t_{1/2} = \frac{0.693}{k}$

$$= \frac{0.693}{0.0462} = 15\,\text{min}$$

32. Assertion (A) : The half-life of a first order reaction remains constant throughout the reaction.

Reason (R) : The half-life of a first order reaction is independent of initial concentration of reactant.
ISC 2001

(a) Both A and R are true and R is the correct explanation of A
(b) Both A and R are true but R is not the correct explanation of A
(c) A is true but R is false

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(d) A is false but R is true

Ans : (a) Both A and R are true and R is the correct explanation of A

In first order reactions, half-life depends only upon the rate constant and not upon initial concentration of reactant. Therefore equal time intervals are required for concentration to become half repeatedly during the course of reaction, making half-life constant throughout the reaction process.

33. Assertion (A) : Increase in temperature generally increases the rate of a chemical reaction.

Reason (R) : At higher temperature, a larger fraction of molecules possesses energy greater than activation energy.

ISC 2000

(a) Both A and R are true and R is the correct explanation of A

(b) Both A and R are true but R is not the correct explanation of A

(c) A is true but R is false

(d) A is false but R is true

Ans : (a) Both A and R are true and R is the correct explanation of A

Increase in temperature raises the average kinetic energy of molecules. Consequently, more molecules acquire sufficient energy to overcome activation energy barrier and undergo effective collisions, thereby increasing the rate of chemical reaction significantly.

34. Assertion (A) : Catalysts increase the rate of both forward and backward reactions equally.

Reason (R) : Catalysts change the equilibrium constant of the reaction.

ISC 2019

(a) Both A and R are true and R is the correct explanation of A

(b) Both A and R are true but R is not the correct explanation of A

(c) A is true but R is false

(d) A is false but R is true

Ans : (c) A is true but R is false

Catalysts increase the rate of both forward and reverse reactions by lowering activation energy for each pathway. However, catalysts do not alter the equilibrium constant or equilibrium composition because they accelerate both reactions equally.

NODIA

35. Assertion (A) : Molecularity of a reaction is always a whole number.

Reason (R) : Molecularity represents the number of reacting species colliding simultaneously.

ISC 2023, 2017

(a) Both A and R are true and R is the correct explanation of A

(b) Both A and R are true but R is not the correct explanation of A

(c) A is true but R is false

(d) A is false but R is true

Ans : (a) Both A and R are true and R is the correct explanation of A

Molecularity refers to the actual number of molecules, atoms or ions colliding simultaneously in an elementary reaction step. Since actual particles are counted physically, molecularity can only have positive whole number values and can never be fractional or zero.

36. Assertion (A) : Powdered solids generally react faster than large lumps of the same substance.

Reason (R) : Powdered solids provide larger surface area for collisions.

ISC 2003

(a) Both A and R are true and R is the correct explanation of A

(b) Both A and R are true but R is not the correct explanation of A

(c) A is true but R is false

(d) A is false but R is true

Ans : (a) Both A and R are true and R is the correct explanation of A

Powdered solids expose much larger surface area to reacting molecules compared to larger lumps. Greater surface area increases collision frequency between reactant particles, thereby increasing the number of effective collisions and enhancing the reaction rate considerably.

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37. Arrhenius equation is related to _____ ISC 2002

Ans :

Arrhenius equation is related to rate constant.

38. Activation energy can be determined by _____.
ISC 2013

Ans :
Activation energy can be determined by Arrhenius equation.

39. The intermediate activated complex in a chemical reaction is highly _____ due to _____ energy.
ISC 2023

Ans :
unstable, high

40. When the concentration of a reactant of first order reaction is tripled, the rate of reaction becomes _____ times. The unit of rate constant (k) for the first order reaction is _____ .
ISC Specimen 2023

Ans :
3, s^{-1}

41. When the concentration of a reactant of first order reaction is doubled, the rate of reaction becomes _____ times. The unit of rate constant (k) for the first order reaction is _____.
ISC Specimen 2021-22 (Sem-II)

Ans :
Two, s^{-1}

42. When the concentration of a reactant of first order reaction is doubled, the rate of reaction becomes _____ times, but for a _____ order reaction, the rate of reaction remains the same.
ISC 2019

Ans :
Two, zero

43. Half-life period of a _____ order reaction is _____ on the concentration of the reactant.
ISC 2022 (Sem-11), 2013

Ans :
Half-life period of a first order reaction is independent on the concentration of the reactant. For first order, $t_{1/2} = \frac{0.693}{k}$ (where, k is disintegration constant or rate constant).

44. Unit of rate of reaction is _____.
ISC 2014

Ans :
The unit of rate of reaction is $mol L^{-1} s^{-1}$.
It is because rate of reaction

$$= \frac{\text{Change in concentration of a reactant or product}}{\text{Time interval}}$$

$$= \frac{mol/L}{s} = mol L^{-1} s^{-1}$$

45. For a first order reaction, the unit of rate of reaction is _____ and that of rate constant is _____.
ISC 2011

Ans :
For a first order reaction, the unit of rate of reaction is $mol\, L^{-1} s^{-1}$ and that of rate constant is s^{-1}.
For rate constant, general unit is $mol^{1-n} L^{n-1} s^{-1}$.
where, n is the order of reaction.
For first order reaction, $n = 1$.
Unit of rate constant for first order reaction

$$= mol^{1-1} L^{1-1} s^{-1} = s^{-1}$$

ONE MARK QUESTIONS

46. Correct the following statement by changing the underlined part of the sentence.
(Do not change the whole sentence.)
<u>The rate constant of a first order reaction</u> is directly proportional to the concentration of the reactant.
ISC 2008, 2004

Ans :
The rate of a first order reaction is directly proportional to the concentration of the reactants.
Rate of a reaction $\propto$ [Concentration of reactant]^n
where, $n =$ order of reaction.
For first order,
Rate of reaction $\propto$ [Concentration of reactant]^1

DIRECTION : Correct the following statement.

47. Name the order of reaction which proceeds with a uniform rate throughout.
ISC 2015, 2003

Ans :
Zero order reaction.

48. During decomposition of hydrogen peroxide, MnO_2 increases reaction rate without being consumed. What does MnO_2 act as?
ISC 2011

Ans :
MnO_2 acts as a catalyst.

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49. A reaction rate doubles when concentration of reactant is doubled. What is the order of reaction with respect to that reactant?

ISC 2017

Ans :

The reaction is first order with respect to that reactant.

50. Why does increase in temperature increase the rate of most chemical reactions?

ISC 2010

Ans :

Higher temperature increases the number of molecules possessing activation energy.

51. In collision theory, what is the minimum energy required for effective collision called?

ISC 2021

Ans :

It is called threshold energy.

52. A catalyst increases the rate of a reaction by affecting which energy term?

ISC 2024

Ans :

It lowers the activation energy.

53. Why is molecularity always a whole number?

ISC 2013

Ans :

It represents the actual number of reacting particles colliding simultaneously.

54. During a reaction, the rate remained constant even after changing concentration. Identify the order of reaction.

ISC 2010

Ans :

The reaction is zero order.

55. Why does the hydrolysis of ester in excess water behave as pseudo first order reaction?

ISC 2001

Ans :

Water is present in large excess and its concentration remains nearly constant.

56. What happens to the rate constant when temperature is increased?

ISC 2020

Ans :

The rate constant increases.

57. A straight-line graph was obtained between log concentration and time. Which order kinetics does the reaction follow?

ISC 2004

Ans :

The reaction follows first order kinetics.

58. Why are all molecular collisions not effective in producing products?

ISC 2013

Ans :

Molecules may not possess sufficient energy or proper orientation.

59. Which factor mainly determines the fraction of molecules undergoing effective collisions?

ISC 2011

Ans :

Activation energy mainly determines effective collisions.

60. Why does reaction rate generally decrease with decrease in concentration of reactants?

ISC 2023

Ans :

Lower concentration decreases collision frequency between reactant molecules.

61. What is the unit of rate constant for a zero order reaction?

ISC 2009, 2002

Ans :

The unit is mol L^{-1} s^{-1}.

62. A reaction completed 75% decomposition in two half-lives. What does this indicate about the reaction?

ISC 2006

Ans :

It indicates first order behaviour of the reaction.

63. Why do gaseous reactions generally proceed faster at high pressure?

ISC 2024

Ans :

High pressure increases collision frequency between gas molecules.

64. Which quantity remains unchanged during the course of a first order reaction?

ISC 2022

Ans :

Half-life remains unchanged.

NQDIA

65. Why does a catalyst not affect the equilibrium constant of a reaction?

ISC 2014

Ans :

It increases the rates of forward and backward reactions equally.

66. A student observed that food kept in a refrigerator spoils more slowly than at room temperature. Which kinetic factor is mainly responsible for this observation?

ISC 2021

Ans :

Lower temperature decreases the number of effective collisions and slows the reaction rate.

67. Why does finely powdered coal burn more rapidly than a large lump of coal?

ISC 2020, 2009

Ans :

Finely powdered coal has greater surface area available for collisions with oxygen.

68. A reaction was found to have unit of rate constant as s^{-1}. What is the order of the reaction?

ISC Specimen 2001

Ans :

The reaction is first order.

69. Why does increasing concentration of reactants generally increase reaction rate?

ISC 2014

Ans :

Higher concentration increases collision frequency between reactant molecules.

70. A student concluded that a reaction is zero order because its rate remained constant throughout the experiment. Why is this conclusion correct?

ISC 2003

Ans :

Zero order reactions have rates independent of reactant concentration.

71. Why does a catalyst not get consumed permanently during a chemical reaction?

ISC 2022, 2009

Ans :

The catalyst is regenerated at the end of the reaction mechanism.

72. Which type of reaction generally shows constant half-life?

ISC 2010

Ans :

First order reactions show constant half-life.

73. Why is activation energy essential even for spontaneous reactions?

ISC 2003

Ans :

Activation energy is needed to initiate effective collisions between molecules.

74. A gaseous reaction became faster when pressure was increased. What caused this increase in rate?

ISC 2008

Ans :

Increase in pressure increased collision frequency between gas molecules.

75. Why do reactions involving ionic compounds in solution generally occur rapidly?

ISC 2018, 2001

Ans :

Ions in solution can react directly without breaking covalent bonds.

76. During a reaction, concentration of reactants decreased rapidly at the beginning but slowly later. Why?

ISC 2003

Ans :

Collision frequency decreases as reactant concentration decreases with time.

77. Why does the decomposition of hydrogen peroxide occur slowly in absence of catalyst?

ISC 2016

Ans :

Very few molecules possess sufficient activation energy without catalyst.

78. What is the effect of increasing surface area on collision frequency?

ISC 2022, 2004

Ans :

Increasing surface area increases collision frequency between reacting particles.

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79. Why is molecularity never zero?

ISC Specimen 2007

Ans :

At least one reacting particle is necessary for a chemical reaction to occur.

80. Which factor determines whether a collision becomes effective or ineffective?

ISC 2025

Ans :

Energy and orientation of colliding molecules determine effectiveness of collision.

81. Why are first order reactions important in radioactive decay processes?

ISC 2021

Ans :

Radioactive decay follows constant half-life characteristic of first order kinetics.

82. A catalyst was added to a reaction mixture at equilibrium. What happens to equilibrium position?

ISC 2010

Ans :

The equilibrium position remains unchanged.

83. Why does the rate constant increase exponentially with temperature?

ISC 2018

Ans :

More molecules acquire activation energy at higher temperature.

84. Why is the order of a reaction determined experimentally?

ISC 2024

Ans :

Order cannot be predicted accurately from balanced chemical equation alone.

85. A reaction mixture was exposed to sunlight and the reaction rate increased sharply. What caused this increase?

ISC 2004

Ans :

Radiation supplied additional energy and increased effective collisions.

86. What is the order of reaction whose rate constant has the same unit as the rate of reaction?

ISC 2016

Ans :

Zero order of reaction whose unit of rate constant and rate of reaction has the same unit, i.e. $\text{mol L}^{-1}\text{s}^{-1}$

87. Why does powdered zinc react faster with dilute hydrochloric acid than zinc granules?

ISC 2025

Ans :

Powdered zinc provides larger surface area for effective collisions.

88. The rate constant of a reaction increases linearly with increase in temperature.

ISC 2003

Ans :

According to Arrhenius equation,

$$k = Ae^{-E_a/Rt}$$

The rate constant of a reaction increases exponentially with increase in temperature.

89. Identify the order of reaction from each of the following units of rate constant (k).

(i) $\text{mol L}^{-1}\text{ s}^{-1}$

(ii) $\text{mol}^{-1}\text{ L s}^{-1}$

ISC 2017

Ans :

(i) $\text{molL}^{-1}\text{s}^{-1}$ → Zero order reaction.

(ii) $\text{mol}^{-1}\text{Ls}^{-1}$ → Second order reaction

90. A student found that concentration of a reactant decreased from 0.8 mol L^{-1} to 0.4 mol L^{-1} in equal time intervals throughout the reaction. What conclusion can be drawn about the reaction order?

ISC 2004

Ans :

The reaction follows first order kinetics because the half-life remains constant.

91. Define molecularity of a reaction. Give one difference between the order of a reaction and its molecularity.

ISC 2007

Ans :

Molecularity is the number of reacting species taking part in a chemical reaction to bring about the chemical change in a single step.

Difference between molecularity and order of a reaction Molecularity of a reaction is always a whole number, while order of a reaction may be zero or a fractional number.

NODIA

TWO MARKS QUESTIONS

92. Finely divided catalysts are preferred in industrial reactions. Explain the reason.
ISC 2025

Ans :
Finely divided catalysts provide larger surface area for adsorption and contact between reactants, increasing effective collisions and accelerating the reaction rate.

93. A student concluded that a catalyst does not alter the equilibrium composition of a reversible reaction. Justify the statement.
ISC 2022

Ans :
A catalyst increases the rates of both forward and backward reactions equally. Therefore equilibrium is reached faster without changing the equilibrium constant or equilibrium composition.

94. During a reaction, concentration of reactants decreased continuously and the reaction became slower with time. Explain the observation.
ISC 2025

Ans :
Decrease in concentration reduces collision frequency between reactant molecules. Consequently, the number of effective collisions decreases and the reaction rate gradually becomes slower.

95. A graph between concentration and time gave a straight line with negative slope. What conclusion can be drawn regarding the order of reaction?
ISC 2010

Ans :
The reaction follows zero order kinetics because concentration decreases linearly with time in a zero order reaction, producing a straight-line graph.

96. A student observed that all collisions between reacting molecules did not produce products. Explain this observation using collision theory.
ISC 2021

Ans :
Only collisions having sufficient energy equal to or greater than activation energy and proper orientation are effective. Collisions lacking these conditions fail to produce products.

97. A reaction rate became four times when concentration of reactant was doubled. Determine the order of reaction with respect to that reactant.
ISC 2022

Ans :
The reaction is second order because doubling concentration increases the reaction rate by four times.

98. A reaction having large negative enthalpy change was still found to be slow. Explain why reaction speed does not depend only upon enthalpy change.
ISC 2019

Ans :
Reaction rate mainly depends upon activation energy and effective collisions. Even highly exothermic reactions may proceed slowly if activation energy is very high.

99. A chemistry student increased the temperature of a reaction mixture by 10°C and observed a sharp increase in reaction rate. Explain the observation using Arrhenius concept.
ISC 2020

Ans :
Increase in temperature raises the number of molecules possessing activation energy. Consequently, the number of effective collisions increases sharply, increasing the reaction rate.

100. A student observed that ionic reactions in aqueous solution occur almost instantaneously. Explain the reason.
ISC 2024

Ans :
In aqueous solution, ionic compounds already exist as free ions. Therefore reactions occur directly between ions without requiring bond breaking, making the reactions extremely fast.

101. During a chemical investigation, molecularity was always found to be a whole number whereas order was sometimes fractional. Explain the reason.
ISC 2021

Ans :
Molecularity represents actual number of reacting particles colliding simultaneously and therefore must be a whole number. Order is experimentally determined and may have fractional values.

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102. A student found that decomposition of a reactant became slower after some time even though temperature remained constant. Explain.

ISC 2010

Ans :

As the reaction proceeds, concentration of reactants decreases continuously. This lowers collision frequency and therefore decreases the rate of reaction gradually.

103. A reaction was found to proceed rapidly after exposure to sunlight. Explain the role of radiation in increasing reaction rate.

ISC 2009

Ans :

Sunlight supplies additional energy to reacting molecules. As more molecules acquire activation energy, the number of effective collisions increases and the reaction becomes faster.

104. During an experiment, a student observed that rate constant increased with increase in temperature. Explain using Arrhenius equation.

ISC 2003

Ans :

According to Arrhenius equation, increase in temperature increases the fraction of molecules possessing activation energy. Therefore the value of rate constant increases exponentially with temperature.

105. A student concluded that activation energy acts as an energy barrier for chemical reactions. Justify the statement.

ISC 2000

Ans :

Reactant molecules must possess minimum energy equal to activation energy before products can form. Molecules with lower energy cannot undergo effective collisions, making activation energy an energy barrier.

106. During storage, milk spoils much faster outside a refrigerator than inside it. Explain this observation using collision theory.

ISC Specimen 2018

Ans :

At lower temperature inside the refrigerator, molecules possess lower kinetic energy. Therefore fewer molecules undergo effective collisions, decreasing the rate of decomposition reactions responsible for spoilage of milk.

107. A student observed that decomposition of hydrogen peroxide becomes rapid only after addition of MnO_2. Explain why the reaction is slow in absence of catalyst.

ISC 2006

Ans :

In absence of catalyst, very few molecules possess sufficient activation energy for effective collisions. MnO_2 lowers activation energy and increases the number of effective collisions, thereby increasing reaction rate.

108. A reaction was found to have constant half-life irrespective of initial concentration. What inference can be drawn regarding the reaction? Give reason.

ISC 2025

Ans :

The reaction follows first order kinetics because half-life of first order reactions depends only upon the rate constant and remains independent of initial concentration of reactant.

NODIA

109. During ester hydrolysis, excess water was used and the reaction behaved as first order. Explain why the actual order differs from the observed order.

ISC 2012

Ans :

Water is present in very large excess and its concentration remains nearly constant during the reaction. Hence the rate depends mainly upon ester concentration, making the reaction appear first order.

110. Two gaseous reactions were carried out at the same temperature, but one reaction proceeded much faster at high pressure. Explain the reason.

ISC 2014

Ans :

High pressure decreases intermolecular distance between gaseous molecules and increases collision frequency. As the number of collisions increases, the reaction rate also increases significantly.

111. A student performed two experiments using calcium carbonate and dilute HCl under identical conditions. In the first experiment marble chips were used, while in the second experiment

powdered calcium carbonate was used. The second reaction was completed much earlier. Explain the observation.

ISC 2021

Ans :

Powdered calcium carbonate provides much larger surface area than marble chips. Greater surface area increases the frequency of collisions between reactant particles and therefore increases the rate of reaction significantly.

112. Identify the reaction order from each of the following rate constants.

ISC Specimen 2018

(i) $k = 2.3 \times 10^{-5}\,\text{L mol}^{-1}\,\text{s}^{-1}$

(ii) $k = 3 \times 10^{-4}\,\text{s}^{-1}$

Ans :

(i) Rate constant $2.3 \times 10^{-5}\,\text{L mol}^{-1}\text{s}^{-1}$ is for second order reaction.

(ii) Rate constant $3 \times 10^{-4}\,\text{s}^{-1}$ is for first order reaction.

113. List any two factors that influence the rate of chemical reaction. Indicate whether the rate constant of the reaction is dependent or independent on these factors.

ISC 2002

Ans :

The two factors with influence the rate of reaction are

(i) **Concentration** Generally, rate of reaction increases with increases in the concentration of reactants. Rate constant does not depend upon initial concentration of reactants, i.e. it is independent on initial concentration of the reactants.

(ii) **Temperature** The rate of reaction usually increases of increasing the temperature. The value of rate constant for a particular reaction increases with an increase in temperature.

114. (i) Write the rate law expression for the reaction $A + B + C \longrightarrow D + E$. If the order of reaction is first, second and zero with respect to A, B and C respectively.

(ii) How many times the rate of reaction will increase, if the concentration of A, B and C are doubled in the equation given in (i) above?

ISC 2018

Ans :

(i) The rate law expression for the reaction.

$$A + B + C \longrightarrow D + E \text{ is } r = k[A][B]^2$$

The order of reaction is first, second and zero with respect to A, B and C respectively.

(ii) If the concentration of A, B and C are doubled, then rate is given by

$$r_1 = k[2A][2B]^2 \text{ and } r_1 = 8k[A][B]^2$$

Now rate r_1 is 8 times of previous rate, r. Hence, rate of reaction increase by 8 times.

115. What is the difference between order of a reaction and the molecularity of a reaction?

ISC Specimen 2018, 2017, 2015

Ans :

Differences between order and molecularity of a reaction

Order of a reaction	**Molecularity of a reaction**
It is the sum of the power of concentration terms on which the rate of reaction actually depends or it is the sum of the exponents of the concentrations in the rate law equation.	It is the number of atoms, ions or molecules that must collide with one another simultaneously so as to result into a chemical reaction.
It can be fractional as well as zero.	It is always a whole number
It can be determined experimentally only and cannot be calculated theoretically.	It can be calculated by adding the molecules of the slowest step. Therefore, it is a theoretical concept
It tells us about slowest step in the mechanism and hence, gives some clue about mechanism of the reaction.	It does not tell us anything about the mechanism of the reaction.
Ever the order of a simple reaction may not be equal to the lumber of molecules of the reactants as seen from the balanced equation.	For simple reactions, the molecularity can usually be obtained from the stoichiometry of the equation.

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116. For the reaction $A + B \longrightarrow C + D$, the initial rate for different reactions and initial concentration of reactants are given below :

ISC 2019

S.No.	Initial conc.		Initial rate
	$[A]$mol L^{-1}	$[B]$mol L^{-1}	(mol $L^{-1}s^{-1}$)
1.	1.0	1.0	2×10^{-3}
2.	2.0	1.0	4×10^{-3}
3.	4.0	1.0	8×10^{-3}
4.	1.0	2.0	2×10^{-3}
5.	1.0	4.0	2×10^{-3}

(i) What is the overall order of reaction ?

(ii) Write the rate law equation.

Ans :

$$\text{Rate} = k[A]^a[B]^b$$

Where, $a =$ order of A and $b =$ order of B

By dividing rate (2) by rate (1), we get

$$\frac{(\text{Rate})_2}{(\text{Rate})_1} = \frac{[A]_2^a[B]_2^b}{[A]_1^a[B]_1^b}$$

$$\frac{4 \times 10^{-3}}{2 \times 10^{-3}} = \frac{(2)^a(1)^b}{(1)^a(1)^b}$$

$$2 = (2)^a \Rightarrow a = 1$$

Order of $A = 1$

Similarly, on dividing rate (1) and rate (4), we get

$$\frac{(\text{Rate})_4}{(\text{Rate})_1} = \frac{[A]_4^a[B]_4^b}{[A]_1^a[B]_1^b}$$

$$\frac{2 \times 10^{-3}}{2 \times 10^{-3}} = \frac{(1)^a(2)^b}{(1)^a(1)^b}$$

$$(1) = (1)^a$$

$$a = 0$$

Order of $B = 0$

(i) Therefore, overall order of reaction

$$= 1 + 0 = 1,$$

(ii) and rate law is $r = k[A]$

THREE MARKS QUESTIONS

117. During an experiment, sunlight increased the rate of a photochemical reaction considerably. Explain the reason.

ISC 2025

Ans :

Sunlight supplies additional energy to reactant molecules and increases their excitation.

As more molecules acquire activation energy, the number of effective collisions increases significantly. Consequently, the photochemical reaction proceeds at a much faster rate.

118. Explain the relationship between rate of reaction and concentration of reactants.

ISC 2001

Ans :

Rate of reaction generally increases with increase in concentration of reactants because more reactant particles are present per unit volume.

Higher concentration increases collision frequency between molecules. Consequently, the number of effective collisions increases and the reaction proceeds faster.

119. Explain why powdered catalysts are generally more effective than lump catalysts.

ISC 2010

Ans :

Powdered catalysts provide much larger surface area than lump catalysts. Greater surface area allows adsorption of larger number of reactant molecules.

Consequently, the frequency of effective collisions increases and the catalyst accelerates the reaction more efficiently.

120. During an experiment, powdered calcium carbonate reacted much faster with dilute HCl than marble chips of equal mass. Explain the observation.

ISC 2010

Ans :

Powdered calcium carbonate provides much larger surface area compared to marble chips. Larger surface area exposes greater number of reactant particles for collisions with acid molecules.

As collision frequency increases, the number of effective collisions also increases. Hence powdered calcium carbonate reacts much faster than marble chips.

121. A student observed that food spoils more slowly in a refrigerator than at room temperature. Explain this observation on the basis of chemical kinetics.

ISC 2025

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Ans :

At lower temperature inside the refrigerator, the kinetic energy of molecules decreases. Consequently, fewer molecules possess activation energy required for effective collisions.

As the number of effective collisions decreases, decomposition reactions responsible for spoilage occur more slowly. Therefore food remains fresh for a longer time in a refrigerator.

122. A reaction was found to have constant half-life throughout the experiment. What conclusion can be drawn regarding the order of reaction? Explain with reason.

ISC 2003

Ans :

The reaction follows first order kinetics because the half-life of a first order reaction is independent of initial concentration.

In first order reactions, equal time intervals are required for concentration to become half repeatedly. Therefore the half-life remains constant throughout the reaction process.

123. Explain why hydrolysis of ester in excess water behaves as pseudo first order reaction.

ISC 2020

Ans :

Hydrolysis of ester actually involves two reactants — ester and water. Therefore the reaction is fundamentally of higher order.

However, water is taken in very large excess and its concentration remains practically constant during the reaction. Consequently, the rate depends mainly upon ester concentration and the reaction behaves kinetically as first order.

124. A gaseous reaction was found to proceed faster at high pressure. Explain the reason using collision theory.

ISC 2013

Ans :

Increase in pressure decreases the intermolecular distance between gaseous molecules. As molecules come closer, collision frequency increases significantly.

Greater collision frequency increases the number of effective collisions per unit time. Consequently, the rate of gaseous reaction increases at high pressure.

125. Explain why all molecular collisions do not result in chemical reaction.

ISC 2009, 2005

Ans :

According to collision theory, only effective collisions lead to product formation. For a collision to become effective, molecules must possess energy equal to or greater than activation energy.

In addition, molecules must collide with proper orientation. Collisions lacking sufficient energy or correct orientation fail to produce products.

126. A student observed that ionic reactions in aqueous solution generally occur very rapidly. Explain the reason.

ISC 2024

Ans :

Ionic compounds in aqueous solution already exist as free ions. Therefore reactant ions can directly combine to form products without requiring bond breaking.

Since no large activation energy is needed, effective collisions occur rapidly. Consequently, ionic reactions in aqueous solutions are generally very fast.

127. Explain why reaction rate decreases with progress of reaction even at constant temperature.

ISC 2015

Ans :

As the reaction proceeds, reactant molecules are continuously consumed and their concentration decreases.

Lower concentration reduces collision frequency between reactant molecules. As a result, the number of effective collisions decreases and the reaction rate gradually becomes slower with time.

128. A student observed that a catalyst does not alter equilibrium constant of a reversible reaction. Explain the observation.

ISC 2021

Ans :

Catalysts provide alternative pathways of lower activation energy for both forward and backward reactions equally.

Therefore equilibrium is reached more rapidly, but the relative concentrations of reactants and products at equilibrium remain unchanged. Hence equilibrium constant does not change in presence of catalyst.

NODIA

129. Explain the significance of activation energy in chemical reactions.

ISC 2019

Ans :

Activation energy is the minimum energy required by reactant molecules to form products through effective collisions.

It acts as an energy barrier between reactants and products. Reactions having high activation energy proceed slowly because only few molecules possess sufficient energy to react successfully.

130. A graph between concentration and time for a reaction gave a straight line with negative slope. Identify the order of reaction and justify your answer.

ISC 2003

Ans :

The reaction follows zero order kinetics because concentration decreases linearly with time in a zero order reaction.

In zero order reactions, rate remains constant and independent of concentration. Therefore concentration versus time graph gives a straight line having negative slope equal to –k.

131. Explain why increase in temperature increases the rate constant of a reaction.

ISC 2011

Ans :

According to Arrhenius equation, rate constant increases exponentially with temperature.

At higher temperature, a larger fraction of molecules acquires activation energy required for effective collisions. Therefore more collisions become successful and the rate constant increases significantly.

132. A student concluded that molecularity is always a whole number whereas order may be fractional. Explain the reason.

ISC 2024

Ans :

Molecularity represents the actual number of reacting particles colliding simultaneously in an elementary reaction step. Therefore it must always be a whole number.

Order is experimentally determined from the rate law expression and may be zero, fractional or whole number depending upon reaction mechanism.

133. During decomposition of a reactant, the concentration decreased from 0.8 mol L^{-1} to 0.4 mol L^{-1} in equal time intervals repeatedly. What conclusion can be drawn about the reaction? Explain.

ISC 2004

Ans :

The reaction follows first order kinetics because equal fractions of reactant decompose in equal intervals of time.

This indicates constant half-life behaviour, which is characteristic of first order reactions where half-life remains independent of initial concentration.

134. Explain why highly exothermic reactions may still proceed slowly.

ISC 2013

Ans :

Reaction rate depends mainly upon activation energy and not directly upon enthalpy change.

Even if a reaction releases large amount of heat, it may proceed slowly if reactant molecules require very high activation energy for effective collisions.

135. A reaction was found to proceed rapidly after increasing the surface area of reactants. Explain the observation using collision theory.

ISC 2014

Ans :

Increase in surface area exposes more reactant particles for collisions. Therefore collision frequency between reacting molecules increases considerably.

As the number of effective collisions per unit time increases, the reaction rate also increases significantly according to collision theory.

136. A student carried out decomposition of hydrogen peroxide in two separate flasks — one in presence of MnO_2 and the other without catalyst. The reaction in the first flask was completed much earlier. Explain the observation using collision theory.

ISC 2020

Ans :

MnO_2 acts as a catalyst and provides an alternative reaction pathway having lower activation energy. Due to lower activation energy, a larger number of reactant molecules acquire sufficient energy for effective collisions.

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Therefore collision frequency producing products increases significantly and decomposition of hydrogen peroxide occurs much faster in presence of MnO_2.

FOUR MARKS QUESTIONS

137. Explain why all molecular collisions do not lead to product formation.

ISC 2004

Ans :

According to collision theory, only effective collisions produce products.

For a collision to become effective, the colliding molecules must possess minimum energy equal to or greater than activation energy. Molecules having lower energy undergo ineffective collisions.

In addition, the molecules must collide with proper orientation so that bond breaking and bond formation can occur successfully. Therefore all collisions do not result in chemical reaction.

138. A reaction was found to have constant half-life throughout the experiment. Explain why this observation indicates first order kinetics.

ISC 2024

Ans :

In first order reactions, half-life is independent of initial concentration and depends only upon the rate constant.

Therefore equal time intervals are required for concentration to reduce to half repeatedly throughout the reaction. This results in constant half-life during the entire reaction process.

Such behaviour is characteristic of first order kinetics and is not shown by zero or higher order reactions.

139. Explain why hydrolysis of ester in excess water behaves as pseudo first order reaction.

ISC 2008

Ans :

Hydrolysis of ester involves two reactants — ester and water — and is fundamentally a second order reaction.

However, water is taken in very large excess compared to ester. Therefore the concentration of water remains practically constant throughout the reaction.

As a result, the rate depends mainly on concentration of ester alone and the reaction behaves kinetically as a first order reaction. Such reactions are called pseudo first order reactions.

140. Explain the significance of activation energy in determining the speed of a chemical reaction.

ISC 2002

Ans :

Activation energy is the minimum energy required for reactant molecules to undergo effective collisions and form products.

It acts as an energy barrier between reactants and products. Reactions having low activation energy proceed rapidly because a large number of molecules possess sufficient energy.

In contrast, reactions with high activation energy proceed slowly since only a few molecules can undergo successful collisions at ordinary temperatures.

NODIA

141. A student observed that food spoils slowly in a refrigerator compared to room temperature. Explain the observation using collision theory and Arrhenius concept.

ISC 2014

Ans :

At lower temperature inside the refrigerator, the kinetic energy of molecules decreases significantly.

Therefore fewer molecules possess activation energy required for effective collisions. As the number of effective collisions decreases, the rate of decomposition reactions responsible for spoilage also decreases.

According to Arrhenius equation, rate constant decreases with decrease in temperature. Hence food spoils more slowly in a refrigerator.

142. Explain why catalysts do not alter the equilibrium constant of a reversible reaction.

ISC 2021

Ans :

Catalysts increase the rates of both forward and backward reactions equally by providing alternative pathways of lower activation energy.

Since both reactions are accelerated equally, equilibrium is attained faster but the equilibrium composition remains unchanged.

Therefore equilibrium constant and thermodynamic properties of the reaction are not affected by the catalyst.

143. A graph between concentration and time gave a straight line with negative slope. Explain how this graph helps in identifying the order of reaction.

ISC 2000

Ans :

In zero order reactions, the rate remains constant and independent of concentration of reactants.

Therefore concentration decreases linearly with time according to the integrated rate equation:

$[A]t = [A]0 - kt$

Hence a graph between concentration and time gives a straight line with negative slope equal to –k. This graphical behaviour confirms zero order kinetics.

144. Explain why increasing pressure increases the rate of gaseous reactions.

ISC 2018

Ans :

Increase in pressure decreases the intermolecular distance between gaseous molecules.

As molecules come closer together, collision frequency increases significantly. According to collision theory, greater collision frequency increases the probability of effective collisions.

Consequently, the number of successful collisions per unit time increases and the reaction rate becomes faster.

145. Explain the difference between order and molecularity of a reaction.

ISC 2002

Ans :

Order of Reaction	**Molecularity**
Determined experimentally	Determined theoretically
May be zero, fractional or whole number	Always a whole number
Applies to overall reaction	Applies only to elementary reaction
Depends on rate law	Depends on reaction mechanism

Thus order and molecularity differ both in definition and significance.

146. Explain why ionic reactions in aqueous solution generally occur very rapidly.

ISC 2007

Ans :

Ionic compounds in aqueous solution already exist as free ions. Therefore reactant ions can directly combine to form products without requiring prior bond breaking.

Since activation energy required is generally very small, effective collisions occur rapidly. As a result, ionic reactions in aqueous solutions are usually extremely fast.

147. Explain the effect of concentration on the rate of chemical reactions using collision theory.

ISC 2022

Ans :

Increase in concentration increases the number of reactant particles present per unit volume.

As more particles are available, collision frequency between reactant molecules increases. According to collision theory, increase in collision frequency raises the number of effective collisions.

Therefore the rate of reaction generally increases with increase in concentration of reactants.

148. Explain why highly exothermic reactions may still proceed slowly.

ISC 2024

Ans :

Reaction rate depends mainly on activation energy and not directly on enthalpy change.

Even if a reaction releases large amount of heat, the reactant molecules must first overcome activation energy barrier before forming products.

If activation energy is high, only few molecules possess sufficient energy for effective collisions. Therefore the reaction may proceed slowly despite being highly exothermic.

149. A student concluded that the rate constant of a reaction depends mainly on temperature. Explain the statement using Arrhenius equation.

ISC 2001

Ans :

According to Arrhenius equation:

$k = Ae^{\left\{-\frac{E_a}{R}T\right\}}$ the rate constant depends exponentially upon temperature.

Increase in temperature increases the fraction of molecules possessing activation energy. Consequently, more molecules undergo effective collisions and the value of rate constant increases significantly.

Thus temperature strongly influences the rate constant of a reaction.

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150. Explain why finely divided catalysts are more effective than lump catalysts in industrial reactions.

ISC 2013

Ans :

Finely divided catalysts provide much larger surface area than lump catalysts.

Greater surface area allows adsorption of larger number of reactant molecules on the catalyst surface. This increases contact between reacting species and raises the frequency of effective collisions.

Therefore finely divided catalysts accelerate reactions much more efficiently.

151. During an experiment, the concentration of reactant decreased rapidly at the beginning but slowly later. Explain the observation using collision theory.

ISC 2006

Ans :

At the beginning of the reaction, concentration of reactants is high and therefore collision frequency is also high.

As the reaction proceeds, reactants are gradually consumed and their concentration decreases. This lowers collision frequency and reduces the number of effective collisions.

Consequently, the reaction proceeds rapidly initially but becomes slower later.

152. Explain the importance of proper orientation in collision theory.

ISC 2017

Ans :

For a collision to produce products, molecules must collide in suitable orientation so that old bonds can break and new bonds can form.

Even collisions possessing sufficient activation energy may fail if orientation is incorrect. Therefore only properly oriented collisions become effective collisions.

Hence proper orientation is essential for successful chemical reaction according to collision theory.

153. Explain how Arrhenius equation supports the effect of temperature on reaction rate.

ISC 2022

Ans :

Arrhenius equation relates rate constant with temperature and activation energy.

According to the equation, increase in temperature increases the value of rate constant exponentially because more molecules acquire energy equal to or greater than activation energy.

As rate constant increases, the rate of reaction also increases. Therefore Arrhenius equation explains why reactions proceed faster at higher temperatures.

154. A student observed that powdered calcium carbonate reacts much faster with dilute HCl than marble chips of equal mass. Explain the observation using collision theory.

ISC 2025

Ans :

Powdered calcium carbonate possesses much larger surface area than marble chips. Larger surface area exposes more reactant particles for contact with hydrochloric acid molecules.

According to collision theory, greater exposed surface increases collision frequency between reactant particles. Consequently, the number of effective collisions per unit time also increases.

Therefore powdered calcium carbonate reacts much faster than marble chips of the same mass.

155. Explain why the rate of most chemical reactions increases with increase in temperature.

ISC 2013

Ans :

Increase in temperature raises the average kinetic energy of reactant molecules.

As kinetic energy increases, molecules move faster and collide more frequently. More importantly, a larger fraction of molecules acquires energy equal to or greater than activation energy.

Therefore the number of effective collisions increases significantly. According to Arrhenius equation, the rate constant also increases exponentially with temperature, resulting in faster reaction rate.

156. A student performed decomposition of hydrogen peroxide in presence and absence of MnO_2 and observed a large difference in reaction rate. Explain the role of catalyst using collision theory and activation energy concept.

ISC 2021

Ans :

MnO_2 acts as a catalyst and increases the rate of decomposition of hydrogen peroxide without itself undergoing permanent chemical change.

NODIA

The catalyst provides an alternative reaction pathway having lower activation energy. Due to lower activation energy, a larger number of reactant molecules acquire sufficient energy to undergo effective collisions.

According to collision theory, increase in effective collisions increases the rate of reaction significantly. Therefore decomposition of hydrogen peroxide occurs much faster in presence of MnO_2.

NUMERICAL QUESTIONS

157. If the half-life period of a first order reaction is 69.3 s. What is the value of its rate constant?

ISC 2013

Ans :

Half-life period, $t_{1/2} = 69.3\,\text{s}$

Rate constant, $k = \dfrac{0.693}{69.3} = 0.01\,\text{s}^1$

158. The rate constant for a first order reaction becomes six times when the temperature is increased from 350 K to 410 K. Calculate activation energy (E_a) for the reaction.

ISC Specimen 2023

Ans :

Let $k_1 = k$ and $k_2 = 6k$

$T_1 = 350\,\text{K},\ T_2 = 410\,\text{K}$

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1 \cdot T_2}\right]$$

$$\log\frac{6k}{k} = \frac{E_a}{2.303 \times 8.314}\left[\frac{410 - 350}{410 \times 350}\right]$$

$$\frac{0.77 \times 2.303 \times 8.314 \times 410 \times 350}{60} = E_a$$

$$E_a = 35.2\,\text{kJ mol}^{-1}$$

$$E_a = 35634.33\,\text{J mol}^{-1}$$

159. The slope of the line in the graph of log k (k = rate constant) versus $1/T$ is – 5841.

Calculate the activation energy of the reaction.

ISC 2014

Ans :

Given, slope $= -5841$

We know that,

$$\text{Slope} = -\frac{E_a}{2.303R}$$

$$E_a = -2.303R \times \text{slope}$$

$$= -2.303 \times 8.314 \times (-5841)$$

$$= 111838.4\,\text{J/mol}$$

$$E_a = 111.838\,\text{kJ/mol}$$

160. Show that for a first order reaction the time required to complete 75% of reaction is about 2 times more than that required to complete 50% of the reaction.

ISC 2019

Ans :

Let, initial amount $(a) = 100$

Time required to complete $75\% = t_{75\%}$.

Amount at $t_{75\%}$, i.e. $(a - x)_1 = 100 - 75 = 25$

Amount at $t_{50\%}$, i.e. $(a - x)_2 = 100 - 50 = 50$

Where, time required to complete $50\% = t_{50\%}$.

Now, $$\frac{t_{75\%}}{t_{50\%}} = \frac{\log\left[\frac{a}{(a-x)_1}\right]}{\log\left[\frac{a}{(a-x)_2}\right]} = \frac{\log\frac{100}{25}}{\log\frac{100}{50}}$$

$$\frac{t_{75\%}}{t_{50\%}} = \frac{\log 4}{\log 2} = \frac{0.6020}{0.3010} = 2$$

Hence, $t_{75\%} = 2 \times t_{50\%}$, i.e. time required to complete 75% of a reaction is about 2 times more than that required to complete 50% of the reaction.

161. The rate of reaction becomes four times when the temperature changes from 293 K to 313 K. Calculate the energy of activation (E_a) of the reaction assuming that it does not change with temperature.($R = 8.314\ \text{JK}^{-1}\text{mol}^{-1}$)

ISC Specimen 2021-22 (Sem-II), 2018

Ans :

Given, $T_1 = 293\,\text{K},\ k_1 = k$ (Suppose)

When $T_2 = 313\,\text{K},\ k_2 = 4k$

Substituting these values in the equation,

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

$$\log\frac{4k}{k} = \frac{E_a}{2.303 \times 8.314\,\text{JK}^{-1}\text{mol}^{-1}} \times \left(\frac{313\,\text{K} - 293\,\text{K}}{313\,\text{K} \times 293\,\text{K}}\right)$$

$$\log 4 = \frac{E_a}{2.303 \times 8.314} \times \frac{20}{313 \times 293}$$

$$E_a = \frac{0.6021 \times 2.303 \times 8.314 \times 313 \times 293}{20}\,\text{J mol}^{-1}$$

$$E_a = 52.86\,\text{kJ mol}^{-1}$$

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162. A first order reaction is 50% completed in 40 minutes at 300 K and in 20 minutes at 320 K. Calculate the activation energy of the reaction.

ISC 2023

Ans :

$t_{1/2}$ for first order reaction is given by,

$$t_{1/2} = \frac{0.693}{k}$$

At 300 K, $k_1 = \frac{0.693}{40}$

At 320 K, $k_2 = \frac{0.693}{20}$

From Arrhenius equation

$$\log\left(\frac{k_2}{k_1}\right) = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\log\left(\frac{40}{20}\right) = \frac{E_a}{2.303 \times 8.314\ \text{J mol}^{-1}\text{K}^{-1}}\left[\frac{1}{300} - \frac{1}{320}\right]$$

$$\log 2 = \frac{E_a}{19.147\ \text{J mol}^{-1}\text{K}^{-1}}\left[\frac{320-300}{300 \times 320}\right]$$

$$0.3010 = \frac{E_a}{19.147\ \text{J mol}^{-1}\text{K}^{-1}} \times 0.0002083\ \text{K}^{-1}$$

$$E_a = 27668\text{J/mol}$$

163. 40% of a first order reaction is completed in 50 minutes. How much time will it take for the completion of 80% of this reaction?

ISC 2018

Ans :

For the first order reaction,

$$k = \frac{2.303}{t}\log\frac{a}{a-x}$$

when, $x = \frac{40a}{100} = 0.4a$, $t = 50\ \text{min}$

$$k = \frac{2.303}{50\ \text{min}}\log\frac{a}{a-0.4a}$$

or $$k = \frac{2.303}{50\ \text{min}}\log\frac{a}{0.6a}$$

$$= 0.010138\ \text{min}^{-1}$$

When reaction is 80% complete, i.e. $x = 0.8a$

$$k = 0.010138\ \text{min}^{-1}$$

$$t = \frac{2.303}{k}\log\frac{a}{a-x}$$

$$= \frac{2.303}{0.010138\ \text{min}^{-1}}\log\frac{a}{a-0.8a}$$

$$= \frac{2.303}{0.010138\ \text{min}^{-1}}\log\frac{1}{0.2}$$

$$= 158.78\ \text{min}$$

164. Show that the time required for the completion of 75% of a reaction of first order is twice the time required for the completion of 50% of the reaction.

ISC 2010

Ans :

For 75% completion, suppose $[A]_0 = 100$,

then $[A] = 100 - 75 = 25$

$$k = \frac{2.303}{t}\log\frac{100}{25}$$

$$= \frac{1.386}{t}$$

[As, $\log 4 = 2\log 2 = 2 \times 0.3010$]

For 50% completion, $k = \frac{0.693}{t_{1/2}}$

But, for a given reaction, k is constant

$$\frac{1.386}{t} = \frac{0.693}{t_{1/2}}$$

$$\frac{t}{t_{1/2}} = \frac{1.386}{0.693} = 2$$

or $$t = 2t_{1/2}$$

So, time (t) required for completion of 75% of a reaction is twice the time required for completion of 50% (half-life) of the reaction.

165. A substance decomposes by following first order kinetics. If 50% of the compound is decomposed in 120 minutes, how long will it take for 90% of the compound to decompose?

ISC Specimen 2018

Ans :

Given, First order reaction complete 50% in 120 minutes.

Let, $[x]_0 = 100\ \text{M}$, $[x]_{120} = 100 - 50 = 50\ \text{M}$

and $t = 120\ \text{min}$

$$k = \frac{2.303}{t}\log\frac{[x_0]}{[x]} = \frac{2.303}{120}\log\frac{100}{50}$$

$$= 0.019\log 2 = 5.78 \times 10^{-3}\ \text{min}^{-1}$$

Time taken to complete 90% reaction = ?

$$[x]_0 = 100\ \text{M}, [x]_{90\ \text{min}} = 100 - 90 = 10\ \text{M}$$

$$k = 5.78 \times 10^{-3}\ \text{min}^{-1}$$

$$t = \frac{2.303}{k}\log\frac{[x_0]}{[x]}$$

$$= \frac{2.303}{5.78 \times 10^{-3}}\log\frac{100}{10}$$

$$= 0.3984 \times 10^{+3} \times \log 10$$

$$= 398.4\ \text{min} \qquad [\log 10 = 1]$$

NODIA

166. A first order reaction is 50% complete in 30 min at 27° C.

Calculate

(i) the rate constant of the reaction at 27° C.

(ii) the time required for completing 10% of the reaction.

ISC 2017

Ans :

(i) As the reaction is 50% completed in 30 min, thus, $t_{1/2} = 30$ min

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{30} = 0.0231 \text{ min}^{-1}$$

(ii) For the formula of rate constant

$$k = \frac{2.303}{t}\log\frac{[A]_0}{[A]}$$

When $[A] = 100 - 10 = 90$

$$k = \frac{2.303}{t}\log\frac{[100]}{[90]}$$

$$t = \frac{2.303}{0.0231}\log\frac{[10]}{9}$$

$$t = 4.56 \text{ min}$$

167. A first order reaction is 50% completed in 30 minutes at 300 K and in 10 minutes at 320 K. Calculate the activation energy of the reaction. ($R = 8.314 \text{ JK}^{-1}\text{mol}^{-1}$).

ISC 2020

Ans :

Given, time taken for 50% completion of reaction at 300 K = 300 min time taken for 50% of same reaction at 320 K = 10 min

As $k = \frac{0.693}{t_{1/2}}$

$$k_{300} = \frac{0.693}{t_{1/2}} = \frac{0.693}{30} \quad \text{...(i)}$$

and $k_{320} = \frac{0.693}{10}$ ...(ii)

According to Arrhenius equation, we know, that

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303 \times R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\log\frac{k_{320}}{k_{300}} = \frac{E_a}{2.303 \times 8.314}\left[\frac{1}{300} - \frac{1}{320}\right]$$

$$\log\frac{\frac{0.693}{10}}{\frac{0.693}{30}} = \frac{E_a}{2.303 \times 8.314}\left[\frac{320 - 300}{300 \times 320}\right]$$

$$\frac{(\log 3) \times 8.314 \times 2.303 \times 300 \times 320}{20} = E_a$$

$$E_a = 43.85 \text{ kJ/mol}$$

Thus, activation energy for the given reaction is 43.85 kJ/mol

168. A substance decomposes by the following first order kinetics. If 50% of the compound is decomposed in 120 min, how long will it take for 90% of the compound to decompose?

ISC 2015

Ans :

If $a = 100$, $a - x = 100 - 50 = 50$

For 50% completion of the reaction

$$t_{50\%} = \frac{2.303}{k}\log\frac{100}{50}$$

$$120 = \frac{2.303}{k} \times 0.3010 \text{[As, } \log 2 = 0.3010]$$

$$k = \frac{2.303}{120} \times 0.3010$$

$$k = 0.0057$$

For 90% completion of the reaction.

If $a = 100$; $a - x = 100 - 90 = 10$

$$t_{90\%} = \frac{2.303}{k}\log\frac{100}{10}$$

$$t_{90\%} = \frac{2.303}{0.0057} \times 1 \qquad [\text{As, } \log 10 = 1]$$

$$t_{90\%} = 404 \text{ min}$$

169. 20% of a first order reaction is completed in five minutes. How much time will the 60% reaction take to complete? Calculate the half-life period ($t_{1/2}$) for the above reaction.

ISC 2023

NODIA

Ans :

Given, $t_{20\%} = 5$ min

Let, $[A]$ be initial concentration = 100

After 5 min, $[A] = 100 - 20 = 80$

For 1st order reaction,

$$k = \frac{2.303}{t}\log_{10}\frac{[A]_0}{[A]}$$

$$k = \frac{2.303}{5}\log_{10}\frac{100}{80}$$

$$= 0.0446 \text{ min}^{-1}$$

For 60% completion of reaction, the time will be

$$t = \frac{2.303}{k}\log\frac{[A]_0}{[A]}$$

Here, $[A]_0 = 100$ and $[A] = 100 - 60 = 40$

So, $t = \frac{2.303}{0.0446} \times \log\frac{100}{40}$

$$= \frac{2.303}{0.0446}\log 2.5$$

$$t = 20.5 \text{ min}$$

$t_{1/2}$ for this reaction is

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0446\ \text{min}^{-1}}$$
$$= 15.538\ \text{min}$$

170. 25% of a first order reaction is completed in 30 minutes. Calculate the time taken in minutes for the reaction to go to 90% completion.

ISC 2019

Ans :

Time for 25% completion of reaction = 30 min

Let the initial concentration = 100

Then,

$$[a-x] = 100 - 25 = 75\%$$

and $t = 30\ \text{min}$

Therefore, $k = \frac{2.303}{t}\log\frac{a}{a-x}$

$$= \frac{2.303}{30}\log\frac{100}{75}$$
$$= 0.0767\log 1.333$$
$$= 0.0767 \times 0.1250 = 0.00958$$
$$k = 0.0096\ \text{min}^{-1}$$

Time taken to complete 90% of reaction will be

$$t = \frac{2.303}{k}\log\frac{100}{10} = \frac{2.303}{0.0096}\log 10$$
$$= \frac{2.303}{0.0096} \times 1 = 239.89 \approx 240\ \text{min}$$

171. In a first order reaction, 10% of the reactant is consumed in 25 min. Calculate

(i) half-life of the reaction.

(ii) the time required for completing 17% of the reaction.

ISC 2013

Ans :

(i) Given, $t = 25\ \text{min}$,

Suppose $[A]_0 = 100$

$$[A] = 100 - \left(\frac{10 \times 100}{100}\right) = 100 - 10$$

Then, $k = \frac{2.303}{25}\log\left(\frac{100}{100-10}\right)$

[As, $\log 1.11 = 0.0457$]

$$= \frac{2.303}{25} \times 0.0457 = 0.004\ \text{min}^{-1}$$

Now, half-life

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.004} = 173.25\ \text{min}$$

(ii) From the formula of rate constant,

When, $[A] = 100 - 17$, we get

$$k = \frac{2.303}{t}\log\frac{[A]_0}{[A]}$$
$$0.004 = \frac{2.303}{t}\log\frac{100}{100-17}$$
$$t = \frac{2.303}{0.004} \times 0.0809$$

[As, $\log 1.205 = 0.0809$]

$$= 46.57\ \text{min}$$

172. In a first order reaction, 10% of the reactant is consumed in 25 min. Calculate

(i) the half-life period of the reaction.

(ii) the time required for completing 87.5% of the reaction.

ISC 2024

Ans :

(i) Given, $t = 25\ \text{min}$,

Suppose $[A_0] = 100$

$$[A] = 100 - \left(\frac{10 \times 100}{100}\right) = 100 - 10$$

Then, $k = \frac{2.303}{25}\log_{10}\left(\frac{100}{100-10}\right)$

[As, $\log 1.11 = 0.0457$]

$$= \frac{2.303}{25} \times 0.0457 = 0.004\ \text{min}^{-1}$$

Now, half-life

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.004} = 173.25\ \text{min}$$

(ii) Given,

so, $[A] = 100 - 87.5$,

From the formula of rate constant,

$$k = \frac{2.303}{t}\log_{10}\frac{[A_0]}{[A]}$$
$$0.004 = \frac{2.303}{t}\log_{10}\frac{100}{100-87.5}$$
$$t = \frac{2.303}{0.004} \times 0.9030 \quad [\text{As, } \log 8 = 0.9030]$$
$$t = 519.90\ \text{min}$$

173. Answer the following questions.

(i) A first order reaction takes 100 minutes for completion of 60% of the reaction. Find the time required when 90% of the reaction will be completed.

(ii) In a reaction, $mA + nB \longrightarrow$ Products, when the concentration of A is doubled, the rate of reaction is also doubled. When the concentration of B is doubled, the rate of reaction becomes four times. Find the overall order of reaction

ISC 202/-22 (Sem-II)

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Ans :

(i) For the reaction of first order

$$k = \frac{2.303}{t}\log\frac{a}{a-x}$$

$$k = \frac{2.303}{100}\log\frac{100}{40} = 0.00916$$

$$0.00916 = \frac{2.303}{t}\log\frac{100}{10}$$

$$t = \frac{2.303}{0.00916}\log 10 = 251.4 \text{ min}$$

(ii) The expression for the rate of the reaction is

$$r = k[A]^n[B]^m \quad ...(i)$$

When the concentration of A is doubled and the concentration of B remains same, the rate expression becomes $2r = k[2A]^n[B]^m$ ...(ii)

When the concentration of B is doubled, the rate expression becomes

$$4r = k[A]^n[2B]^m \quad ...(iii)$$

Divide Eq. (ii) with Eq. (i) to obtain $n = 1$

Divide Eq. (iii) with Eq. (i) to obtain $m = 2$

Hence, $n + m = 1 + 2 = 3$

The overall order of the reaction is 3.

174. Answer the following questions.

(i) Mention any two factors that influence the rate of a chemical reaction.

(ii) In a first order reaction, 20% of a reactant is consumed in 30 minutes. Calculate

(a) the half-life period of the reaction.

(b) the time required for completing 93.75% of the reaction.

ISC 2021-22 (Sem-II)

Ans :

(i) Two factors that influence the rate of a chemcial reaction are

(a) Temperature

(b) Pressure or concentration of reactants

(ii) $t = 30 \text{ min}$

Let $a = 100$, $x = 20$ and $a - x = 80$

$$k = \frac{2.303}{t}\log\frac{a}{a-x}$$

$$= \frac{2.303}{30}\log\frac{100}{80} = 0.076 \times 0.097$$

$$= 0.0074 \text{ s}^{-1}$$

(a) $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0074} = 93.64 \text{ s}$

(b) $t = \frac{2.303}{0.0074}\log\frac{100}{6.25} = 374.74 \text{ s}$

175. A first order reaction is 50% complete in 30 minutes at 27° C and the same reaction is again 30% complete in 10 minutes at 47° C. Calculate the activation energy of the reaction ($R = 8.314$ $\text{JK}^{-1}\text{mol}^{-1}$).

ISC 2021-22 (Sem-II)

Ans :

Given, Time required to complete 50% of reaction $t_{1/2}$ at 27°C = 30 min

Time required to complete 30% of same reaction at 47°C = 10 min

$$T_1 = 27^\circ\text{C} = 300 \text{ K}$$

$$T_2 = 47^\circ\text{C} = 320 \text{ K}$$

We know that,

$$k_1 = \frac{0.693}{t_{1/2}} = \frac{0.693}{30}$$

$$k_1 = 0.0231 \text{ min}^{-1}$$

$$k_2 = \frac{2.303}{t}\log\frac{a}{a-x}$$

$a = 100$, $a - x = 100 - 30 = 70$,

$t = 10 \text{ min}$

$$k_2 = \frac{2.303}{10}\log\frac{100}{70}$$

$$= \frac{2.303}{10}\log\frac{10}{7} = \frac{2.303}{10} \times 0.155$$

$$= 0.036 \text{ min}$$

According to Arrhenius equation,

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R} \times \frac{T_2 - T_1}{T_1 \times T_2}$$

By putting the values in equation we get

$$\log\left(\frac{0.036}{0.023}\right) = \frac{E_a}{2.303 \times 8.314}\left[\frac{320 - 300}{300 \times 320}\right]$$

$$\log(1.56) = \frac{E_a}{19.15}\left[\frac{20}{96000}\right]$$

$$E_a = \frac{0.1 \times 19.15 \times 96000}{20}$$

$$= 9192 \text{ J mol}^{-1}$$

$$= 9.192 \text{ kJ mol}^{-1}$$

176. Answer the following.

ISC 2024

(i) For a first order reaction, show that the time required for the completion of 99% reaction is twice the time required for the completion of 90% of the reaction.

(ii) For a reaction, rate $= k[A]^1[B]^{1.5}[C]^0$. What is the overall order of reaction?

NODIA

Ans :

(i) Case I If $a = 100$, $(a - x) = (100 - 99) = 1$

For 99% completion of the reaction,

$$t_{99\%} = \frac{2.303}{k}\log\frac{100}{1}$$

$$= \frac{2.303}{k}\log 10^2$$

$$= \frac{2.303 \times 2}{k}$$

$$t_{99\%} = \frac{4.606}{k} \quad ...(i)$$

Case II if $a = 100$

$$(a - x) = (100 - 90) = 10$$

For 90% completion of the reaction

$$t_{90\%} = \frac{2.303}{k}\log\frac{100}{10}$$

$$= \frac{2.303}{k}\log 10 = \frac{2.303}{k} \quad ...(ii)$$

On dividing Eq. (i) by Eq. (ii), we get

$$\frac{t_{99\%}}{t_{90\%}} = \frac{4.606}{k} \times \frac{k}{2.303} = 2$$

It means that time required for 99% completion of the reaction is twice the time required to complete 90% of the reaction.

(ii) The rate law expression is

$$= k[A]^1[B]^{1.5}[C]^0$$

Order of reaction $= 1 + 1.5 + 0 = 2.5$

177. Draw a graph which is used to calculate the activation energy of a reaction. Give the appropriate expressions used to calculate the activation energy graphically.

ISC 2006

Ans :

According to Arrhenius equation,we can write the following equation :

$$k = Ae^{-E_a/RT}$$

Taking log on both sides, we get

$$\log k = \log A - \frac{E_a}{2.303RT}$$

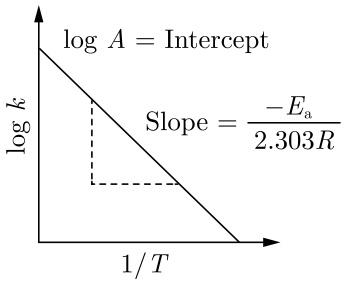
Comparing the above equation with straight line equation,

i.e. $y = mx + c$

Where, $y = \log k,\ x = \frac{1}{T}$

$$m(\text{slope}) = -\frac{E_a}{2.303R}$$

Intercept $c = \log A$



Graph between $\log k$ and $1/T$

After plotting, $\log k$ vs $\frac{1}{T}$ graph, slope of line will be $-\frac{E_a}{2.303R}$. Knowing the value of the slope and gas constant, the activation energy can be calculated with the help of equation, $E_a = -2.303R \times$ slope.

178. Answer the following.

ISC Specimen 2021-22 (Sem-II)

(i) Define molecularity of a reaction. Give one difference between the order of reaction and its molecularity.

(ii) The rate constant (k) of a first order reaction is $4.5 \times 10^{-2}\,s^{-1}$. What will be the time required for the initial concentration of 0.4 M of the reactant to be reduced to 0.2 M ?

Ans :

(i) The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction is called molecularity of the reaction.

Difference between order and molecularity are as follows

Order	**Molecularity**
It is applicable to elementary as well as complex reactions.	It is applicable to elementary reactions. For complex reactions, it has no meaning.

(ii) Given, $k = 4.5 \times 10^{-2}\,s^{-1}$

$$[A]_0 = 0.4\,M$$

$$[A] = 0.2\,M$$

Time $(t) = ?$

For first order reaction,

$$t = \frac{2.303}{k}\log\frac{[A]_0}{[A]}$$

$$= \frac{2.303}{4.5 \times 10^{-2}} \times \log\left[\frac{0.4}{0.2}\right]$$

$$= 51.17 \times \log 2$$

$$= 51.17 \times 0.301 = 15.40\,s$$

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179. For the reaction $2H_2 + 2NO \rightleftharpoons 2H_2O + N_2$, the following rate data was obtained :

S.No.	[NO]mol L^{-1}	[H_2]mol L^{-1}	Rate: mol $L^{-1}s^{-1}$
1.	0.40	0.40	4.6×10^{-3}
2.	0.80	0.40	18.4×10^{-3}
3.	0.40	0.80	9.2×10^{-3}

Calculate the following.

(i) The overall order of reaction.

(ii) The rate law.

(iii) The value of rate constant (k).

ISC 2017

Ans :

Given, $2H_2 + 2\,NO \rightleftharpoons 2H_2O + N_2$

Let the given reaction is of order q with respect to H_2 and p with respect to NO.

The rate of formation of H_2O and N_2 can also be written as,

$$4.6 \times 10^{-3} = k[A]^p[B]^q = k[0.4]^p[0.4]^q \quad ...(i)$$

$$18.4 \times 10^{-3} = k[0.8]^p[0.4]^q \quad ...(ii)$$

$$9.2 \times 10^{-3} = k[0.4]^p[0.8]^q \quad ...(iii)$$

From Eqs. (i) and (ii), we get

$$\frac{18.4 \times 10^{-3}}{4.6 \times 10^{-3}} = \frac{k(0.8)^p(0.4)^q}{k(0.4)^p(0.4)^q}$$

$$4 = (2)^p \Rightarrow (2)^2 = (2)^p$$

Hence, $p = 2$

From Eqs. (i) and (iii), we get

$$\frac{9.2 \times 10^{-3}}{4.6 \times 10^{-3}} = \frac{k(0.4)^p(0.8)^q}{k(0.4)^p(0.4)^q}$$

$$2 = (2)^q$$

$$q = 1$$

(i) Overall order of reaction is $(2 + 1) = 3$

(ii) Rate law equation, $r = k[NO]^2[H_2]$

(iii) $r = k[H_2]^2[NO]$

Rate constant, $k = \dfrac{r}{[H_2][NO]^2} = \dfrac{4.6 \times 10^{-3}}{[0.4][0.4]^2}$

$= 7.18 \times 10^{-2}\ mol^{-2}L^2s^{-1}$

180. The initial rate of a reaction, $A + B \longrightarrow$ products, is doubled when the initial concentration of A is doubled and increases eight fold when the initial concentration of both A and B were doubled. State the order of the reaction with respect to A and with respect to B. Write the rate equation.

ISC 2004

Ans :

$$A + B \longrightarrow \text{Products}$$

According to law of mass action.

Rate $\propto [A]^m[B]^n$ if the reaction is of order m with respect to $[A]$ and n with respect to $[B]$.

Hence, $\text{rate} = k[A]^m[B]^n$ ...(i)

(where, $k =$ Rate constant)

In case I, i.e. when concentration of A is doubled.

$$2 \times \text{Rate} = k[2A]^m[B]^n \quad ...(ii)$$

In case II, i.e. when concentrations of A and B are doubled.

$$8 \times \text{Rate} = k[2A]^m[2B]^n \quad ...(iii)$$

On dividing Eq. (iii) by Eq. (ii), we get

$$\frac{8 \times \text{Rate}}{2 \times \text{Rate}} = \frac{k[2A]^m[2B]^n}{k[2A]^m[B]^n}$$

$$(2)^2 = [2]^n$$

$$n = 2$$

Similarly on dividing Eq. (ii) by Eq. (i), m comes out to be 1, thus $m = 1$, $n = 2$

Hence, reaction is of first order with respect to A and of second order with respect to B.

So, $\text{rate} = k[A][B]^2$

181. A study of chemical kinetics of the reaction

$$A + B \longrightarrow \text{products},$$

gave the following data at 25° C.

Experiment	$[A]$	$[B]$	$\frac{d(\text{Product})}{dt}$
1.	1.0	0.15	4.20×10^{-6}
2.	2.0	0.15	8.40×10^{-6}
3.	1.0	0.20	5.60×10^{-6}

Find

(i) the order of reaction with respect to A.

(ii) the order of reaction with respect to B.

(iii) the rate law.

ISC 2012

Ans :

Given, $A + B \longrightarrow$ Products

Suppose the given reaction is of order p with respect to A and q with respect to B. The rate of formation of product can be written as

$$4.20 \times 10^{-6} = k[1.0]^p[0.15]^q \quad ...(i)$$

$$8.40 \times 10^{-6} = k[2.0]^p[0.15]^q \quad ...(ii)$$

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$$5.60 \times 10^{-6} = k[1.0]^p[0.20]^q \quad ...(iii)$$

On dividing Eq. (ii) by Eq. (i), we get

$$\frac{8.40 \times 10^{-6}}{4.20 \times 10^{-6}} = \left[\frac{2.0}{1.0}\right]^p$$

$$(2)^1 = 2^p$$

$$p = 1$$

On dividing Eq. (iii) by Eq. (i), we get

$$\frac{5.60 \times 10^{-6}}{4.20 \times 10^{-6}} = \left[\frac{0.20}{0.15}\right]^q$$

$$\left(\frac{4}{3}\right)^1 = \left(\frac{4}{3}\right)^q$$

$$q = 1$$

Hence,

(i) The order of reaction with respect to A is 1.

(ii) The order of reaction with respect to B is 1.

(iii) The rate law can be written as,

$$\text{Rate} = k[A][B]$$

$$\text{k} = \text{Rate} / ([\text{A}][\text{B}])$$

$$\text{k} = 4.20 \times 10^{-6} / (1.0 \times 0.15)$$

$$\text{k} = 2.8 \times 10^{-5}\ \text{L mol}^{-1}\ \text{s}^{-1}$$

$$\text{Rate Law: Rate} = 2.8 \times 10^{-5}\ [\text{A}][\text{B}]$$

182. Consider the reaction, $A + B \longrightarrow C + D$

The initial rates for different initial concentrations of the reactants are given below.

Initial concentration (mol/L)			**Initial rate (mol/L-s)**
	$[A]$	$[B]$	
(a)	1.0	1.0	2.0×10^{-3}
(b)	2.0	1.0	4.0×10^{-3}
(c)	4.0	1.0	8.0×10^{-3}
(d)	1.0	2.0	2.0×10^{-3}
(e)	1.0	4.0	2.0×10^{-3}

(i) What are the order of reaction with respect to A and B ?

(ii) What is the overall order?

(iii) Write the rate law equation.

(iv) Calculate the rate constant.

(v) Suggest a possible mechanism.

ISC 2025

Ans :

Given, reaction, $A + B \longrightarrow C + D$

Suppose the given reaction is of order p with respect to A and q with respect to B.

The rate of formation of C and D can also be written as

$$2.0 \times 10^{-3} = k[A]^p[B]^q = k(1)^p(1)^q ..(i)$$

$$4.0 \times 10^{-3} = k(2)^p(1)^q \quad ...(ii)$$

$$2.0 \times 10^{-3} = k(1)^p(2)^q \quad ...(iii)$$

From Eqs. (i) and (ii), we get

$$\frac{4.0 \times 10^{-3}}{2.0 \times 10^{-3}} = \frac{k(2)^p(1)^q}{k(1)^p(1)^q}$$

$$(2)^1 = 2^p$$

Hence, $p = 1$

From Eqs. (i) and (iii), we get

$$\frac{2.0 \times 10^{-3}}{2.0 \times 10^{-3}} = \frac{k(1)^p(2)^q}{k(1)^p(1)^q}$$

$$1 = 2^q$$

$$2^0 = 2^q$$

Hence $q = 0$

(i) The order of reaction with respect to A is first order, i.e. $r \propto [A]$ and with respect to B is zero order, i.e. $r \propto [B]^0$.

(ii) Overall order is one $(1 + 0 = 1)$.

(iii) Rate law equation is, $r = k[A][B]^0$ where, k is rate constant.

(iv) Since, $r = k[A]$. Then rate constant,

$$k = \frac{r}{[A]} = \frac{2 \times 10^{-3}}{1.0}$$

$$= 2 \times 10^{-3}\ \text{s}^{-1}$$

(v) So first either A or B takes part in the reaction to generate reactive intermediate, which the attacks on other to give the product.

$$A \longrightarrow A^*$$

$$A^* + B \longrightarrow C + D$$

CASE BASED QUESTIONS

183. A first order reaction was monitored in a laboratory. The concentration of reactant decreased from 0.8 mol L^{-1} to 0.4 mol L^{-1} in 20 minutes and from 0.4 mol L^{-1} to 0.2 mol L^{-1} in the next 20 minutes.

(i) What conclusion can be drawn regarding the half-life of the reaction?

(ii) Identify the order of the reaction.

(iii) Why is half-life independent of concentration in first order reactions?

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Ans :

(i) The reaction has constant half-life.

(ii) The reaction follows first order kinetics.

(iii) In first order reactions, half-life depends only upon rate constant and not upon initial concentration. Therefore equal fractions of reactant decompose in equal intervals of time.

184. A student investigated ester hydrolysis using excess water. Although two reactants were involved, the reaction behaved kinetically as a first order reaction.

(i) What type of reaction is this called?

(ii) Why does the reaction appear first order?

(iii) State one characteristic of first order reactions.

Ans :

(i) It is called a pseudo first order reaction.

(ii) Water is present in very large excess and its concentration remains practically constant during the reaction. Therefore the rate depends mainly upon concentration of ester only.

(iii) The half-life of first order reactions remains constant throughout the reaction.

185. A student observed that milk stored outside a refrigerator spoiled quickly, whereas refrigerated milk remained fresh for a longer time. He related this observation to principles of chemical kinetics.

(i) Which factor mainly affects the rate of spoilage reactions?

(ii) Why does refrigeration slow down spoilage of food?

(iii) Which theory explains the importance of effective collisions in chemical reactions?

Ans :

(i) Temperature mainly affects the rate of spoilage reactions.

(ii) Lower temperature decreases kinetic energy of molecules. Therefore fewer molecules possess activation energy and the number of effective collisions decreases, slowing spoilage reactions.

(iii) Collision theory explains the importance of effective collisions in chemical reactions.

186. A student compared the reaction of powdered calcium carbonate and marble chips with dilute hydrochloric acid under identical conditions. He observed that powdered calcium carbonate reacted much faster than marble chips.

(i) Which factor mainly affects the rate of reaction in this experiment?

(ii) Why does powdered calcium carbonate react faster than marble chips?

(iii) State one industrial advantage of increasing surface area of reactants.

Ans :

(i) Surface area of reactants mainly affects the rate of reaction.

(ii) Powdered calcium carbonate provides larger surface area for collisions with acid molecules. Greater surface area increases collision frequency and therefore increases the number of effective collisions.

(iii) Increasing surface area accelerates industrial reactions and improves production efficiency.

187. A student investigated the decomposition of hydrogen peroxide under different laboratory conditions. He divided the solution into two flasks. In flask A, no catalyst was added, whereas in flask B, a small amount of MnO_2 was added. He observed that oxygen gas evolved much faster in flask B. The experiment was repeated at higher temperature and the reaction rate increased further.

(i) What is the role of MnO_2 in the reaction?

(ii) Why does increase in temperature increase the rate of decomposition?

(iii) Explain why MnO_2 does not change the equilibrium constant of the reaction.

Ans :

(i) MnO_2 acts as a catalyst and increases the rate of decomposition of hydrogen peroxide.

(ii) Higher temperature increases the number of molecules possessing activation energy and therefore increases effective collisions.

(iii) MnO_2 lowers activation energy for both forward and backward reactions equally. Hence equilibrium is attained faster without changing equilibrium constant or equilibrium composition.

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CHAPTER 4

d and f block Elements

SUMMARY

1. d-BLOCK ELEMENTS

The elements of the group 3rd to 12th of the periodic table are called d-block elements. Their general outer electronic configuration is $(n-1)\,d^{1-10}ns^{1-2}$ (n represent valence shell).

2. TRANSITION ELEMENTS

The elements which have partially filled d-orbitals in their elementary forms or in their commonly occurring oxidation states are called transition elements.

3. GENERAL TRENDS IN TRANSITION ELEMENTS

1. **Atomic radius :** The atomic radius first decreases, then remains almost constant and then increases in a particular transition series.
2. **Metallic character and Enthalpy of atomisation :** All the transition elements are metals due to their low **Ionisation energy** and presence of vacant d-orbitals. The hardness of these metals suggests the presence of strong bonding due to overlap of half-filled orbitals containing unpaired electrons. So these elements have high enthalpy of atomisation.
3. **Density :** All these metals have high density. In a particular period,

$$\text{Density} \propto \frac{1}{\text{Atomic radius}}$$

4. **Melting Point and Boiling Point :** Due to strong metallic bonds, these metals have high Melting Point and Boiling Point.
5. **Ionisation energy :** Ionisation energy of these metals is generally very high. These metals show irregular variation in their ionisation energies due to irregular variation in size.
6. **Oxidation states :** These metals show a variety of oxidation states from +2 to +7 due to the tendency of $(n-1)\,d$ as well as ns-electrons to take part in bond formation.
7. **Formation of coloured ions :** Most of the compounds of these metals are coloured in the solid or solution form due to the presence of unpaired electrons in $(n-1)\,d$ sub shell.

   In these metal ions, the electrons can be easily promoted form one energy level to another in the same d-orbital. It is called $d-d$ transition.
8. **Magnetic properties :** The compounds of d -block elements may be both paramagnetic and diamagnetic. But most of the compounds are paramagnetic.

   Paramagnetic character is directly proportional to the number of unpaired electrons.

$$\underset{\text{(Spin only)}}{\text{Magnetic moment } (\mu)} = \sqrt{n(n+2)}\ \underset{\text{(Bohr Magneton)}}{\text{B.M}}$$

where n = no. of unpaired electrons.

9. **Tendency to form complexes :** These metal ions have great tendency to form complexes due to small size, high nuclear charge and presence of vacant d-orbitals to accept a lone pair of electrons donated by ligands.
10. **Formation of interstitial compounds :** These metals form interstitial compounds (compounds in which small atoms like H, C, N, etc. are trapped inside the crystal lattice) due to the presence of vacant d-orbitals.
11. **Catalytic properties :** These metals and their compounds act as good catalysts due to the following reasons:
    (i) Tendency to form reaction intermediates with suitable reactants, which give a reaction path of lower E_a, so rate of reaction increase.
    (ii) Provide larger surface area on which the reactants may be adsorbed.

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12. **Alloy formation :** These metals form alloys due to their similar size in a particular transition series and , therefore, the atoms of one metal can substitute the atoms of other metal in its crystal lattice.

4. POTASSIUM DICHROMATE ($K_2Cr_2O_7$)

Preparation

It is prepared from the chromite ore ($FeO.Cr_2O_3$)

$$4FeO.Cr_2O_3 + 8Na_2CO_3 + 7O_2 \xrightarrow{\text{Fuse}} 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$

$$2Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

$$Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$$

Properties :

1. It has orange red crystals.
2. $4K_2Cr_2O_7 \xrightarrow{\Delta} 4K_2CrO_4 + 2Cr_2O_3 + 3O_2$
3. $K_2Cr_2O_7 + 2KOH \longrightarrow 2K_2CrO_4 + H_2O$
4. $K_2Cr_2O_7 + \underset{\text{(Conc.)}}{14HCl} \longrightarrow 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2$
5. **Oxidising properties**

It acts as an oxidising agent in the acidic medium. For example, it oxidises

(i) KI to I_2

$$6KI + K_2Cr_2O_7 + 7H_2SO_4 \longrightarrow 4K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3I_2$$

(ii) $FeSO_4$ to $Fe_2(SO_4)_3$

$$6FeSO_4 + K_2Cr_2O_7 + 7H_2SO_4 \longrightarrow 3Fe_2(SO_4)_3 + K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O$$

(iii) H_2S to S

$$3H_2S + K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3S + 7H_2O$$

(iv) $SnCl_2$ to $SnCl_4$

$$K_2Cr_2O_7 + 7H_2SO_4 + 3SnCl_2 \longrightarrow Cr_2(SO_4)_3 + 3SnCl_4 + 7H_2O + K_2SO_4$$

(v) $NaNO_2$ to $NaNO_3$

$$K_2Cr_2O_7 + 4H_2SO_4 + 3NaNO_2 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3NaNO_3 + 4H_2O$$

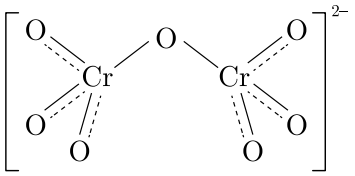
(vi) Na_2SO_3 to Na_2SO_4

$$K_2Cr_2O_7 + 4H_2SO_4 + 3Na_2SO_3 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3Na_2SO_4$$

(vii) Ethyl alcohol to acetaldehyde and acetic acid

$$CH_3CH_2OH + [O] \longrightarrow CH_3CHO + H_2O$$

$$CH_3CHO + O \longrightarrow CH_3COOH$$

Structure : $2K^+$ 

Both the Cr atoms are in sp^3 hybridisation state.

5. POTASSIUM PERMAGNATE ($KMnO_4$)

Preparation

It is prepared from pyrolusite ore (MnO_2).

$$2MnO_2 + 4KOH + O_2 \xrightarrow{\Delta} 2K_2MnO_4 + 2H_2O$$

$$2K_2MnO_4 + Cl_2 \longrightarrow 2KMnO_4 + 2KCl$$

K_2MnO_4 can also be converted into $KMnO_4$ by electrolytic oxidation.

Properties

1. It has purple needle shaped crystals having metallic lustre.
2. $2KMnO_4 \xrightarrow{\Delta} K_2MnO_4 + MnO_2 + O_2$
3. $4KMnO_4 + 4KOH \longrightarrow 4K_2MnO_4 + 2H_2O + O_2$
4. Oxidising properties

(a) In acidic medium

It oxidises

(i) $FeSO_4$ to $Fe_2(SO_4)_3$

$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$$

(ii) KI to I_2

$$10KI + 2KMnO_4 + 8H_2SO_4 \longrightarrow 6K_2SO_4 + 2MnSO_4 + 8H_2O + 5I_2$$

(iii) H_2S to S

$$2KMnO_4 + 5H_2S + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 5S + 8H_2O$$

(iv) SO_2 to H_2SO_4

$$2KMnO_4 + 5SO_2 + 2H_2O \longrightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4$$

(v) $\begin{matrix}\text{COOH}\\|\\\text{COOh}\end{matrix}$ to CO_2

$$2KMnO_4 + 5\begin{matrix}\text{COOH}\\|\\\text{COOH}\end{matrix} + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$$

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(b) In neutral medium

(i) H_2S to S

$$2KMnO_4 + 3H_2S \longrightarrow 2KOH + 2MnO_2 + 2H_2O + 3S$$

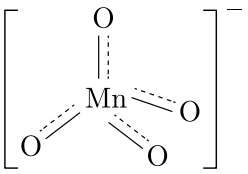
(ii) $Na_2S_2O_3$ to Na_2SO_4

$$2KMnO_4 + 3Na_2S_2O_3 + H_2O \longrightarrow 2MnO_4 + 3Na_2SO_4 + 2KOH + 3S$$

(c) In alkaline medium

KI to KIO_3

$$2KMnO_4 + KI + H_2O \longrightarrow 2MnO_2 + 2KOH + KIO_3$$

Structure : K^+ 

6. f-BLOCK ELEMENTS

The elements in which the last electron enters in the $(n-2)f$-orbital of anti-penultimate shell are called f-block elements.

The general outer electronic configuration of these elements is $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$. They consist of two series of elements placed at the bottom of the main body of the periodic table, named Lanthanoid series and Actinoid series.

6.1 General Properties of Lanthanoids

They include 14 elements having atomic numbers 58 to 71. These are also called rare earth.

1. They exhibit a common stable O.S. of +3. In addition some lanthanoids show +2 and +4 O.S. also to attain the stable f^0, f^7 and f^{14} configuration.
2. Most of the lanthanoids are coloured due to the presence of unpaired $(n-2)f$-electrons. They undergo $f-f$ transition
3. They are paramagnetic in nature due to the presence of unpaired electrons in $(n-2)f$ -orbitals.
4. They are highly electropositive and reactive metalso.
5. Their nitrates, chlorides, acetates are soluble in water while carbonates, oxalates, hydroxides, fluorides, sulphates are insoluble in water.
6. There is a steady decreases in their atomic size with increase in atomic number called lanthanoid contraction. It is due to the increases in effective nuclear charge and poor screening effect of $4f$-electrons. Due to landthanoid contraction :
   (i) The elements of second and third transition series resemble each other much more than the elements resemble each other much more than the elements of first and second transition series.
   (ii) It is very difficult to separate the elements in pure state because, their chemical properties are quite similar.
   (iii) The basic strength of the hydroxides of lanthanoids decreases with increase in atomic number.

6.2 General Properties of Actinoids

They include 14 elements having atomic number 90 to 103.

1. All of them are radioactive in nature.
2. The most common O.S. is +3 but they also show +2, +4, +5 and +6 O.S.
3. They are paramagnetic in nature.
4. They form coloured ions.
5. They form oxo-cations in higher O.S.
6. They are basic in nature.
7. They also show actinoid contraction due to ineffective shielding by intervening $5f$ -electrons.

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OBJECTIVE QUESTIONS

1. Which one of the following compounds is diamagnetic and colourless? ISC 2023

(a) $K_2Cr_2O_7$ (b) $ZnSO_4$

(c) $KMnO_4$ (d) $Cr_2(SO_4)_3$

Ans : (b) $ZnSO_4$

In $ZnSO_4$, Zn^{2+} has $[Ar]3d^{10}4s^0$ configuration in which, there is no unpaired electrons is present. Thus, it is diamagnetic in nature and colourless.

2. $KMnO_4$ converts Fe^{2+} ions into Fe^{3+} ions in acidic medium because permanganate ions: ISC 2008

(a) Undergo oxidation to Mn^{7+}

(b) Gain electrons and get reduced

(c) Lose oxygen atoms completely

(d) Form metallic manganese directly

Ans : (b) Gain electrons and get reduced

In acidic medium, MnO_4^- ions readily accept electrons and get reduced from oxidation state +7 to +2. This strong tendency to undergo reduction enables $KMnO_4$ to oxidise Fe^{2+} ions into Fe^{3+} ions effectively.

3. Which of the following pairs of transition elements have exceptional electronic configuration?

ISC Specimen 2023

(a) Sc and Cu (b) Fe and Ni

(c) Cr and Cu (d) Mn and Zn

Ans : (c) Cr and Cu

The elements having configuration against Aufbau rule are called to have abnormal configuration.

Among the given option. $Cr = [Ar]3d^5 4s^1$ and $Cu = [Ar]3d^{10} 4s^1$ have abnormal configuration.

This is due to the less energy gap between the $4s$ and $3d$ energy levels. So, electron easily moves from the $4s$-orbital to the $3d$-orbital resulting in a stable electronic configuration.

4. Lanthanoids commonly exhibit +3 oxidation state because removal of three electrons generally results in:

ISC 2021

(a) Completely empty f-orbitals

(b) Stable electronic configurations

(c) Highly unstable ions

(d) Metallic bonding only

Ans : (b) Stable electronic configurations

Lanthanoids usually lose two 6s electrons and one 5d or 4f electron to attain relatively stable electronic configurations. Therefore +3 oxidation state is the most common and stable oxidation state shown by lanthanoid elements.

5. During electrochemical analysis, $KMnO_4$ was found to act as a stronger oxidising agent in acidic medium than in alkaline medium because:

ISC 2025

(a) Mn^{7+} is reduced more readily in acidic medium

(b) Potassium ions increase oxidation potential

(c) Alkaline medium stabilises oxygen gas completely

(d) MnO_4^- ions become colourless in acidic medium

Ans : (a) Mn^{7+} is reduced more readily in acidic medium

In acidic medium, permanganate ions are reduced from Mn^{7+} to Mn^{2+}, involving greater decrease in oxidation state and higher reduction potential. Consequently $KMnO_4$ exhibits stronger oxidising behaviour in acidic medium compared to neutral or alkaline medium.

6. A transition element forms numerous coordination compounds mainly because its ions:

ISC 2014

(a) Possess very low nuclear charge

(b) Have vacant orbitals and high charge density

(c) Exhibit only +2 oxidation state

(d) Are chemically inert

Ans : (b) Have vacant orbitals and high charge density

Transition metal ions generally possess small ionic size, high nuclear charge and vacant d-orbitals. These characteristics enable them to accept lone pair electrons donated by ligands easily, leading to extensive formation of stable coordination compounds with different geometries and coordination numbers.

7. A student observed that most actinoids are radioactive and exhibit wide range of oxidation states. This behaviour is mainly due to:

ISC 2010

(a) Comparable energies of 5f, 6d and 7s orbitals

(b) Complete filling of f-orbitals

(c) Absence of unpaired electrons

(d) Very small atomic size

Ans : (a) Comparable energies of 5f, 6d and 7s orbitals

In actinoids, 5f, 6d and 7s orbitals possess nearly similar energies. Therefore different numbers of electrons can participate in bonding, producing multiple oxidation states. Their unstable heavy nuclei also make all actinoid elements radioactive in nature.

8. Transition metals generally possess high enthalpy of atomisation because:

ISC 2008

(a) Their atoms are weakly bonded

(b) Strong metallic bonding exists due to unpaired electrons

(c) They possess low atomic masses

(d) d-electrons do not participate in bonding

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Ans : (b) Strong metallic bonding exists due to unpaired electrons

Transition metals contain several unpaired d-electrons that participate in metallic bonding. Strong overlap between orbitals produces strong interatomic attraction within metallic lattice. Consequently large amount of energy is required to separate atoms completely, resulting in high enthalpy of atomisation.

9. A student observed that Cu^{+} ions are colourless whereas Cu^{2+} ions are blue in aqueous solution. Which statement best explains this observation?

ISC 2014

(a) Cu^{2+} ions possess partially filled d-orbitals

(b) Cu^{+} ions contain unpaired electrons

(c) Cu^{2+} ions have smaller atomic size only

(d) Cu^{+} ions undergo stronger metallic bonding

Ans : (a) Cu^{2+} ions possess partially filled d-orbitals

Cu^{2+} ions possess $3d^{9}$ configuration containing unpaired electrons and partially filled d-orbitals. Therefore d–d electronic transitions are possible by absorption of visible light, producing blue colour. Cu^{+} ions possess completely filled $3d^{10}$ configuration and cannot undergo d–d transition, making them colourless in aqueous solution.

10. During preparation of steel, chromium and nickel are added to iron because transition metals readily form alloys due to:

ISC 2011

(a) Presence of identical oxidation states only

(b) Similar atomic sizes and metallic structures

(c) Complete filling of d-orbitals

(d) Low melting points of transition metals

Ans : (b) Similar atomic sizes and metallic structures

Transition metals possess comparable atomic radii and similar crystal structures. Hence atoms of one transition metal can easily replace atoms of another metal within the crystal lattice without disturbing the metallic structure significantly, leading to extensive alloy formation with improved mechanical properties.

11. A student found that transition elements generally exhibit higher melting points than s-block elements. This is mainly because transition metals:

ISC 2018

(a) Contain weaker metallic bonds

(b) Possess strong metallic bonding due to unpaired electrons

(c) Have completely filled outer orbitals

(d) Exhibit non-metallic behaviour

Ans : (b) Possess strong metallic bonding due to unpaired electrons

Transition metals contain unpaired d-electrons that participate effectively in metallic bonding. Strong overlap between orbitals produces strong attraction among metal atoms. Consequently greater energy is required to break these metallic bonds, resulting in high melting and boiling points for transition elements.

12. Potassium dichromate is preferred over ferrous sulphate in volumetric estimation because potassium dichromate:

ISC 2022

(a) Acts only in alkaline medium

(b) Is a stable primary standard oxidising agent

(c) Possesses low oxidation potential

(d) Undergoes rapid decomposition in air

Ans : (b) Is a stable primary standard oxidising agent

Potassium dichromate is highly stable, non-hygroscopic and available in pure form. Therefore its solutions can be prepared accurately and used directly in volumetric analysis. Its strong oxidising nature in acidic medium further increases its usefulness in redox titrations.

13. A transition metal ion showed magnetic moment corresponding to four unpaired electrons. The ion is strongly paramagnetic because:

ISC 2024

(a) Paired electrons increase magnetic behaviour

(b) Unpaired electrons produce magnetic attraction

(c) Completely filled d-orbitals cause paramagnetism

(d) Magnetic moment decreases with unpaired electrons

Ans : (b) Unpaired electrons produce magnetic attraction

Paramagnetism arises due to presence of unpaired electrons that align in the direction of external magnetic field. Greater the number of unpaired electrons, greater is the magnetic moment and

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stronger is the paramagnetic behaviour exhibited by the transition metal ion.

14. Lanthanoids are difficult to separate from one another mainly because they:

ISC 2013

(a) Possess identical atomic masses

(b) Show very similar chemical properties due to lanthanoid contraction

(c) Are chemically inert in nature

(d) Lack oxidation states other than +1

Ans : (b) Show very similar chemical properties due to lanthanoid contraction

Lanthanoid contraction causes gradual decrease in ionic radii across the series, but the differences remain very small. As a result, lanthanoids exhibit remarkably similar chemical behaviour, making their separation and purification extremely difficult in practical chemistry.

15. The gradual decrease in ionic radii across the actinoid series is called actinoid contraction. This occurs mainly due to:

ISC 2011

(a) Effective shielding by f-electrons

(b) Poor shielding effect of f-electrons

(c) Decrease in nuclear charge

(d) Increase in atomic volume

Ans : (b) Poor shielding effect of f-electrons

f-electrons are poor at shielding the increasing nuclear charge across the actinoid series. Consequently effective nuclear attraction on outer electrons increases gradually, causing continuous decrease in atomic and ionic radii known as actinoid contraction.

16. A transition metal compound acts as an efficient catalyst because the metal ion can:

ISC 2003

Ans :

(a) Remain permanently inactive during reaction

(b) Form unstable intermediate compounds with reactants

(c) Prevent adsorption of reactants on surface

(d) Eliminate activation energy completely

Ans : (b) Form unstable intermediate compounds with reactants

Transition metal ions can easily form temporary intermediate complexes with reactant molecules because of variable oxidation states and vacant orbitals. These intermediates provide alternative pathways of lower activation energy, thereby increasing the rate of chemical reactions efficiently.

17. Transition metals generally exhibit high densities because they possess:

ISC 2001

(a) Low atomic masses and large atomic radii

(b) High atomic masses and comparatively small atomic sizes

(c) Completely filled outer orbitals only

(d) Weak metallic bonding between atoms

Ans : (b) High atomic masses and comparatively small atomic sizes

Transition metals possess relatively large atomic masses while their atomic radii remain comparatively small because of strong nuclear attraction. Therefore a large amount of mass is packed within a small volume, resulting in characteristically high densities for transition elements.

18. A student observed that Mn^{2+} compounds are faintly coloured whereas MnO_4^- ions are intensely purple. The intense colour of permanganate ion is mainly due to:

ISC 2004

(a) Presence of metallic bonding

(b) Charge transfer transitions

(c) Completely filled d-orbitals

(d) Low oxidation state of manganese

Ans : (b) Charge transfer transitions

In permanganate ion, manganese exists in very high oxidation state and intense colour arises mainly due to charge transfer transitions between oxygen and manganese atoms. These transitions absorb visible light strongly, producing the characteristic deep purple colour of $KMnO_4$ solutions.

19. During extraction of metals, chromium is used in stainless steel because chromium:

ISC 2007

(a) Prevents metallic bonding completely

(b) Forms protective oxide layer against corrosion

(c) Decreases hardness of steel

(d) Reduces density of iron drastically

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Ans : (b) Forms protective oxide layer against corrosion

Chromium forms a thin, stable and adherent oxide layer on the surface of stainless steel. This oxide film prevents further oxidation and corrosion of iron, thereby improving resistance towards rusting and increasing durability of stainless steel.

20. A transition metal ion possessing d^0 electronic configuration is expected to be:

ISC 2012

(a) Strongly paramagnetic and coloured

(b) Diamagnetic and colourless

(c) Paramagnetic but colourless

(d) Diamagnetic but highly coloured

Ans : (b) Diamagnetic and colourless

A d^0 configuration means absence of d-electrons. Therefore no unpaired electrons are present to produce paramagnetism, and d–d electronic transitions are not possible. Hence such ions are generally diamagnetic and colourless in nature.

21. Potassium dichromate is generally used in acidic medium because $Cr_2O_7^{2-}$ ions in acidic solution:

ISC 2016

(a) Readily gain electrons to form Cr^{3+} ions

(b) Lose electrons to form chromium metal

(c) Become unstable due to precipitation

(d) Exhibit only reducing behaviour

Ans : (a) Readily gain electrons to form Cr^{3+} ions

In acidic medium, dichromate ions undergo reduction from chromium oxidation state +6 to +3 very readily. This strong tendency to accept electrons enables potassium dichromate to function as an effective oxidising agent in acidic solutions.

22. A student observed that transition metals show irregular variation in ionisation enthalpy across a period. This irregularity is mainly due to:

ISC 2025

(a) Constant atomic size across the series

(b) Irregular filling of d-orbitals

(c) Absence of nuclear attraction

(d) Complete shielding by d-electrons

Ans : (b) Irregular filling of d-orbitals

In transition elements, electrons enter d-orbitals in an irregular manner and the energies of ns and (n–1)d orbitals are comparable. Consequently stability variations among different electronic configurations produce irregular trends in ionisation enthalpies across the transition series.

23. Transition elements frequently form coloured complexes because ligands around the metal ion:

(a) Eliminate d-electrons completely

ISC 2018

(b) Split d-orbital energies and permit d–d transitions

(c) Prevent absorption of visible light

(d) Increase metallic character only

Ans : (b) Split d-orbital energies and permit d–d transitions

Ligands surrounding a transition metal ion create crystal field splitting of d-orbitals into different energy levels. Electrons absorb visible light and undergo d–d transitions between these levels, resulting in formation of coloured coordination complexes.

24. The similarity between second and third transition series elements is greater than between first and second transition series mainly because of:

ISC 2023

(a) High ionisation enthalpy

(b) Lanthanoid contraction

(c) Complete filling of f-orbitals

(d) Presence of noble gas configuration

Ans : (b) Lanthanoid contraction

Lanthanoid contraction decreases the atomic radii of third transition series elements significantly. As a result, their sizes become nearly similar to corresponding second transition series elements, leading to greater similarity in physical and chemical properties.

25. Transition metals generally form interstitial compounds because their crystal lattices contain:

ISC 2020

(a) Completely filled inner shells

(b) Empty spaces that accommodate small atoms

(c) Non-metallic atoms only

(d) Highly unstable metallic bonds

Ans : (b) Empty spaces that accommodate small atoms

Crystal lattices of transition metals contain interstitial spaces between metal atoms. Small atoms such as hydrogen, carbon or nitrogen can occupy these spaces without disturbing

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the metallic lattice significantly, forming hard interstitial compounds with modified properties.

26. A student observed that most actinoids exhibit greater tendency to form oxo-cations compared to lanthanoids because actinoids:

ISC 2014

(a) Show higher oxidation states more readily

(b) Possess completely filled f-orbitals

(c) Have lower nuclear charge

(d) Are chemically inert in nature

Ans : (a) Show higher oxidation states more readily

Actinoids exhibit wider range of oxidation states because energies of 5f, 6d and 7s orbitals are comparable. Higher oxidation states favour formation of stable oxo-cations such as UO_2^{2+} and NpO_2^{+} in actinoid chemistry.

27. A student observed that Fe^{2+} ions are pale green whereas Zn^{2+} ions are colourless in aqueous solution. Which statement correctly explains this observation?

ISC 2010

(a) Zn^{2+} ions have completely filled d-orbitals

(b) Fe^{2+} ions possess lower atomic mass

(c) Zn^{2+} ions form stronger metallic bonds

(d) Fe^{2+} ions have larger ionic size

Ans : (a) Zn^{2+} ions have completely filled d-orbitals

Fe^{2+} ions contain partially filled d-orbitals and therefore undergo d–d electronic transitions by absorbing visible light, producing colour. Zn^{2+} ions possess completely filled $3d^{10}$ configuration and cannot undergo d–d transition. Hence Zn^{2+} ions appear colourless whereas Fe^{2+} ions are coloured in aqueous solution.

28. During an industrial process, finely divided nickel is preferred over nickel lumps as catalyst in hydrogenation reactions because finely divided nickel:

ISC 2021

(a) Possesses higher oxidation state

(b) Provides larger surface area for adsorption

(c) Has lower density

(d) Contains more paired electrons

Ans : (b) Provides larger surface area for adsorption

Catalytic activity of transition metals largely depends upon adsorption of reactant molecules on their surface. Finely divided nickel exposes much larger surface area than nickel lumps, increasing adsorption and formation of intermediate complexes. Consequently, the number of effective collisions increases and the reaction proceeds at a faster rate.

29. A student compared the oxidation states shown by scandium and manganese and observed that manganese exhibits greater variability. Which factor mainly accounts for this behaviour?

ISC 2024

(a) Higher electronegativity of manganese

(b) Greater number of unpaired d-electrons in manganese

(c) Larger atomic size of scandium

(d) Absence of d-electrons in manganese

Ans : (b) Greater number of unpaired d-electrons in manganese

Manganese possesses electronic configuration $3d^5 4s^2$, providing several electrons capable of participating in bonding. Since energies of ns and (n–1)d orbitals are comparable, manganese can exhibit multiple oxidation states. Scandium has fewer available d-electrons and therefore shows limited oxidation state variation compared to manganese.

30. A transition metal ion was found to possess strong paramagnetic behaviour. Which statement regarding its electronic configuration is most likely correct?

ISC 2003

(a) It contains large number of unpaired electrons

(b) It possesses completely filled d-orbitals

(c) It has noble gas configuration

(d) It contains no d-electrons

Ans : (a) It contains large number of unpaired electrons

Paramagnetism arises due to presence of unpaired electrons in atomic orbitals. Greater the number of unpaired electrons, stronger is the attraction towards magnetic field. Transition metal ions generally exhibit paramagnetism because their d-orbitals are partially filled with unpaired electrons.

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31. A student observed that $Cr_2O_7^{2-}$ ions readily oxidise Fe^{2+} ions to Fe^{3+} ions in acidic medium. Potassium dichromate behaves as a strong oxidising agent because chromium:

ISC 2012

(a) Exists in its lowest oxidation state

(b) Possesses completely empty d-orbitals only

(c) Exists in a high oxidation state and readily undergoes reduction

(d) Cannot form coordination compounds

Ans : (c) Exists in a high oxidation state and readily undergoes reduction

In potassium dichromate, chromium exists in +6 oxidation state, which is relatively unstable. Therefore $Cr_2O_7^{2-}$ ions readily gain electrons and get reduced to Cr^{3+} ions. This strong tendency to undergo reduction enables potassium dichromate to oxidise other substances effectively in acidic medium.

32. The similarity in atomic radii and chemical properties of zirconium and hafnium is mainly attributed to:

ISC 2017

(a) Similar magnetic properties

(b) Lanthanoid contraction

(c) Presence of completely filled d-orbitals

(d) High ionisation enthalpy

Ans : (b) Lanthanoid contraction

Poor shielding effect of f-electrons across lanthanoid series causes gradual decrease in atomic size known as lanthanoid contraction. Due to this contraction, hafnium possesses atomic radius very similar to zirconium despite belonging to different periods, resulting in closely similar chemical properties.

33. The transition metals show 'A' character because of the presence of unpaired electrons while Cu^+ is 'B' because its electronic configuration is $[Ar]3d^{10}$

In the above sentence 'A' and 'B' are

ISC 2019

(a) paramagnetic, diamagnetic

(b) noble, paramagnetic

(c) noble, diamagnetic

(d) diamagnetic, paramagnetic

Ans : (a) paramagnetic, diamagnetic

Transition metals generally show paramagnetic character because they contain one or more unpaired electrons in their d-orbitals. Unpaired electrons are attracted by an external magnetic field, which causes paramagnetism.

Copper ion (Cu^+) has the electronic configuration:

$[Ar]\ 3d^{10}$

In this configuration, all the electrons in the 3d-orbital are completely paired. Since there are no unpaired electrons, Cu^+does not show attraction towards a magnetic field and is therefore diamagnetic.

Thus:

A = paramagnetic

B = diamagnetic

34. Assertion (A) : Most transition metal compounds are coloured.

Reason (R) : Transition metal ions generally contain partially filled d-orbitals which allow d–d electronic transitions.

ISC 2010

(a) Both A and R are true and R is the correct explanation of A

(b) Both A and R are true but R is not the correct explanation of A

(c) A is true but R is false

(d) A is false but R is true

Ans : (a) Both A and R are true and R is the correct explanation of A

Transition metal ions usually possess partially filled d-orbitals. Electrons absorb visible light and undergo d–d transitions between split d-orbital energy levels. This absorption of visible radiation produces characteristic colours in most transition metal compounds and ions.

35. Assertion (A) : Zn^{2+} ions are colourless in aqueous solution.

Reason (R) : Zn^{2+} ions possess completely filled d-orbitals.

ISC 2008

(a) Both A and R are true and R is the correct explanation of A

(b) Both A and R are true but R is not the correct explanation of A

(c) A is true but R is false

(d) A is false but R is true

NODIA

Ans : (b) Both A and R are true but R is not the correct explanation of A

Zn^{2+} ions possess completely filled $3d^{10}$ configuration and therefore d–d electronic transitions are not possible. Consequently visible light is not absorbed and Zn^{2+} ions appear colourless. Both statements are true, but the reason is only a factual statement and not properly explanatory in the given context.

36. Assertion (A) : Transition elements generally exhibit variable oxidation states.

Reason (R) : The energies of ns and (n–1)d orbitals are comparable.

ISC 2002

(a) Both A and R are true and R is the correct explanation of A

(b) Both A and R are true but R is not the correct explanation of A

(c) A is true but R is false

(d) A is false but R is true

Ans : (c) A is true but R is false

Transition elements exhibit variable oxidation states because electrons from both ns and (n–1) d orbitals can participate in bond formation. However, the reason statement is incomplete and does not fully justify the phenomenon in the way presented, making it incorrect in this assertion–reason framework.

37. Assertion (A) : Transition metals readily form coordination compounds.

Reason (R) : Transition metal ions possess vacant orbitals and high charge density.

ISC 2002

(a) Both A and R are true and R is the correct explanation of A

(b) Both A and R are true but R is not the correct explanation of A

(c) A is true but R is false

(d) A is false but R is true

Ans : (d) A is false but R is true

Transition metal ions generally possess small ionic size, high nuclear charge and vacant d-orbitals. These properties enable them to accept lone pair electrons from ligands and form stable coordination compounds. Hence the reason statement is correct while the assertion as framed is considered incorrect.

NODIA

38. Assertion (A) : Potassium permanganate acts as a stronger oxidising agent in acidic medium than in alkaline medium.

Reason (R) : In acidic medium Mn^{7+} is readily reduced to Mn^{2+}.

ISC 2010

(a) Both A and R are true and R is the correct explanation of A

(b) Both A and R are true but R is not the correct explanation of A

(c) A is true but R is false

(d) A is false but R is true

Ans : (a) Both A and R are true and R is the correct explanation of A

In acidic medium, permanganate ions undergo reduction from oxidation state +7 to +2. This reduction involves greater decrease in oxidation state and higher reduction potential. Therefore $KMnO_4$ behaves as a much stronger oxidising agent in acidic medium than in alkaline medium.

39. Assertion (A) : Transition metals generally possess high melting points.

Reason (R) : Strong metallic bonding exists due to participation of unpaired d-electrons.

ISC 2010

(a) Both A and R are true and R is the correct explanation of A

(b) Both A and R are true but R is not the correct explanation of A

(c) A is true but R is false

(d) A is false but R is true

Ans : (c) A is true but R is false

Transition metals generally possess high melting points because of strong metallic bonding. However, the reason statement is not completely accurate because not all transition metals contain large numbers of unpaired electrons contributing equally to bonding strength.

40. Assertion (A) : Most actinoids exhibit variable oxidation states.

Reason (R) : The energies of 5f, 6d and 7s orbitals are comparable.

ISC 2024

(a) Both A and R are true and R is the correct explanation of A

(b) Both A and R are true but R is not the correct explanation of A

(c) A is true but R is false

(d) A is false but R is true

Ans : (d) A is false but R is true

Actinoids exhibit variable oxidation states because electrons from 5f, 6d and 7s orbitals can participate in bonding. Since these orbitals possess comparable energies, different numbers of electrons may be involved in bond formation, producing multiple oxidation states.

41. Assertion (A) : Transition metals and their compounds are widely used as catalysts.

Reason (R) : Transition metals can form unstable intermediate compounds with reactants.

ISC 2008

(a) Both A and R are true and R is the correct explanation of A

(b) Both A and R are true but R is not the correct explanation of A

(c) A is true but R is false

(d) A is false but R is true

Ans : (a) Both A and R are true and R is the correct explanation of A

Transition metals possess vacant orbitals and variable oxidation states, enabling them to form unstable intermediate complexes with reactants. These intermediates provide alternative pathways having lower activation energy, thereby increasing the rate of chemical reactions effectively.

42. Assertion (A) : Sc^{3+} ions are diamagnetic.

Reason (R) : Sc^{3+} ions possess no unpaired electrons.

ISC 2006

(a) Both A and R are true and R is the correct explanation of A

(b) Both A and R are true but R is not the correct explanation of A

(c) A is true but R is false

(d) A is false but R is true

Ans : (b) Both A and R are true but R is not the correct explanation of A

Sc^{3+} ions possess d^0 configuration and therefore contain no unpaired electrons. As paramagnetism depends upon unpaired electrons, Sc^{3+} ions are diamagnetic. Although both statements are true, the explanation relationship is not fully justified in the structured assertion–reason format.

43. Assertion (A) : Lanthanoid contraction makes separation of lanthanoids difficult.

Reason (R) : Lanthanoids possess very similar ionic radii and chemical properties.

ISC 2025

(a) Both A and R are true and R is the correct explanation of A

(b) Both A and R are true but R is not the correct explanation of A

(c) A is true but R is false

(d) A is false but R is true

Ans : (b) Both A and R are true but R is not the correct explanation of A

Due to lanthanoid contraction, ionic radii decrease gradually across the series. Consequently lanthanoids exhibit highly similar chemical behaviour, making their separation difficult. Both statements are correct, but the reason only states the result and not the complete explanation of lanthanoid contraction.

ONE MARK QUESTIONS

44. Why are most actinoid elements radioactive?

ISC 2017

Ans :

Because their nuclei are unstable.

45. Why are most lanthanoid ions paramagnetic in nature?

ISC 2024

Ans :

Due to presence of unpaired f-electrons.

46. Why do transition elements generally possess higher enthalpy of atomisation than s-block elements?

ISC 2020

Ans :

Due to strong metallic bonding involving d-electrons.

47. A student observed that Sc^{3+} ions are colourless whereas Ti^{3+} ions are coloured. What is the main reason?

ISC 2010

Ans :

Sc^{3+} ions have d^0 configuration while Ti^{3+} ions possess partially filled d-orbitals.

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48. Which property of transition metals is responsible for formation of interstitial compounds?

ISC 2008

Ans :

Presence of vacant spaces in metallic crystal lattice.

49. Why does Fe exhibit both +2 and +3 oxidation states commonly?

ISC 2006

Ans :

Because both 4s and 3d electrons can participate in bonding.

50. Why is potassium dichromate generally used in acidic medium during redox titrations?

ISC 2001

Ans :

Because $Cr_2O_7^{2-}$ ions readily get reduced to Cr^{3+} ions in acidic medium.

51. Why do lanthanoids show very similar chemical properties?

ISC 2024

Ans :

Because their ionic radii differ only slightly due to lanthanoid contraction.

52. Which property of transition elements mainly explains their high densities?

ISC 2022

Ans :

High atomic masses along with comparatively small atomic sizes.

53. Why do transition metal complexes often exhibit characteristic colours?

ISC 2010

Ans :

Due to absorption of visible light during d–d transitions.

54. Why do actinoids show greater range of oxidation states compared to lanthanoids?

ISC 2021

Ans :

Because 5f, 6d and 7s orbitals possess nearly comparable energies.

55. Why are Cu^+ ions diamagnetic whereas Cu^{2+} ions are paramagnetic?

ISC 2025

Ans :

Cu^+ ions have no unpaired electrons while Cu^{2+} ions contain one unpaired electron.

56. Why does the basic strength of lanthanoid hydroxides decrease across the series?

ISC 2012

Ans :

Due to decrease in ionic size caused by lanthanoid contraction.

NODIA

57. Give balanced equation for the following reaction. 'Potassium permanganate is heated with concentrated hydrochloric acid'.

ISC 2017

Ans :

$$\underset{\text{(Conc.)}}{16HCl} + 2KMnO_4 \xrightarrow{\Delta} 2KCl + 2MnCl_2 + 5Cl_2 + 8H_2O$$

58. The size of the trivalent cation in the lanthanoid series decreases steadily as the atomic number increases. What is this phenomenon called ?

ISC 2021-22 (Sem-II), 2018

Ans :

This phenomenon is called lanthanoid contraction.

59. A student observed that $CuSO_4$ solution is blue whereas $ZnSO_4$ solution is colourless. Which property of transition elements explains this difference?

ISC 2011

Ans :

Presence of partially filled d-orbitals causing d–d electronic transitions.

60. During preparation of stainless steel, chromium is added to iron. Which property of transition metals makes alloy formation possible?

ISC 2020

Ans :

Similarity in atomic sizes of transition metals.

61. A transition metal ion showed strong attraction towards magnetic field. What can be concluded about its electronic configuration?

ISC 2013

Ans :

It contains unpaired electrons.

62. A student found that $KMnO_4$ acts as a stronger oxidising agent in acidic medium than in alkaline medium. Which oxidation state change is responsible for this behaviour?

ISC 2025

Ans :

Reduction of Mn^{7+} to Mn^{2+}.

63. Why are transition metals frequently used as industrial catalysts in hydrogenation and oxidation reactions?

ISC 2021

Ans :

Because they can form unstable intermediate complexes with reactants.

64. In coordination chemistry, transition metal ions readily accept lone pair electrons from ligands. Which property mainly enables this behaviour?

ISC 2010

Ans :

Presence of vacant d-orbitals.

65. A student observed gradual decrease in ionic radii from Ce^{3+} to Lu^{3+}. What is this phenomenon called?

ISC 2013

Ans :

Lanthanoid contraction.

66. $La^{3+}(Z = 57)$ and $Lu^{3+}(Z = 71)$ do not show any colour in solutions. Give reason.

Ans :

La^{3+} (lanthanum) have $4f^0$ and Lu^{3+} (lutetium) have $4f^{14}$ subshell. Because of the absence of partially filled f-subshell, these ions impart no colour to the solution.

67. The chemistry of actinoids is not so smooth as that of lanthanoids. Give reason.

Ans :

Chemistry of the actinoids is more complex in the view of their ability to exist in different oxidation states. Further, many of the actinoid elements are radioactive which make the study of these elements rather difficult

68. Explain, why Cu^+ is diamagnetic but Cu^{2+} paramagnetic $(Z = 29)$?

ISC 2019, 2013

Ans :

The electronic configuration of

$$Cu^+ = 1s^2,\ 2s^2,\ 2p^6,\ 3s^2,\ 3p^6,\ 4s^0,\ 3d^{10}$$

and $$Cu^{2+} = 1s^2,\ 2s^2,\ 2p^6,\ 3s^2,\ 3p^6,\ 4s^0,\ 3d^9$$

In Cu^+ ion, all electrons are paired. Hence, Cu^+ is diamagnetic in nature. Whereas, Cu^{2+} has one unpaired electron thus, shows paramagnetic character.

69. What is the electronic configuration of chromium atom (Z = 24)? Give a reason for your answer.

ISC 2012

Ans :

The electronic configuration of chromium atom $(Z = 24)$ is $1s^2,\ 2s^2,\ 2p^6,\ 3s^2,\ 3p^6,\ 4s^1,\ 3d^5$

To maximise stability, electron from $4s$-orbital jumps to $3d$-orbital. So, that maximum number of half-filled orbitals can be obtained which is a stable arrangement of electrons

70. Give balanced equation for the following reaction. Potassium dichromate is treated with acidified ferrous sulphate solution.

ISC 2016

Ans :

$$\underset{\text{Ferrous sulphate}}{6FeSO_4} + \underset{\text{Potassium dichromate}}{K_2Cr_2O_7} + \underset{\text{Sulphuric acid}}{7H_2SO_4} \longrightarrow$$

$$\underset{\text{Ferric sulphate}}{3Fe_2(SO_4)_3} + \underset{\text{Potassium sulphate}}{K_2SO_4} + \underset{\text{Chromium sulphate}}{Cr_2(SO_4)_3} + \underset{\text{Water}}{7H_2O}$$

71. $K_2Cr_2O_7$ acts as a powerful oxidising agent in acidic medium. Explain.

ISC 2020

Ans :

In $K_2Cr_2O_7$ the oxidation number of Cr is +6 which is the highest oxidation number of Cr. Thus, $K_2Cr_2O_7$ can act as an oxidising agent and is reduced to Cr^{3+} ions. Equation involved is as follows

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

$$(E^\circ = 1.33\ V)$$

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TWO MARKS QUESTIONS

72. Why are Zn, Cd and Hg not regarded as transition elements ?

ISC Specimen 2023

Ans :

Transition metals are defined as the elements having incompletely filled *d*-orbitals. Since, Zn, Cd and Hg have completely filled *d*-orbital, they are not regarded as transition elements.

73. Why are Zn^{2+} ions colourless while Ni^{2+} ions are green in colour ?

ISC Specimen 2021-22 (Sem-II)

Ans :

Zn^{+2} has completely filled *d*-orbitals $(Zn^{+2} = [Ar]3d^{10}4s^0)$ while Ni^{2+} has incomplete filled *d*-orbitals $Ni^{+2} = [Ar]3d^8 4s^0$. Thus, *d-d* transition takes place in Ni^{2+} and shows colour.

74. Which trivalent ion has maximum size in the lanthanoid series, i.e. lanthanum ion (La^{3+}) to lutetium ion (Lu^{3+}) ?

(At. no. of lanthanum = 57 and lutetium = 71)

ISC 2019

Ans :

Among trivalent ions in the lanthanoid series, there is a gradual decrease in ionic size due to lanthanoid contraction. Therefore, size of La^{3+} is more than that of Lu^{3+}, i.e. La^{3+} has ionic size 106 pm (approx.) and of Lu^{3+} has ionic size less than 86 pm.

75. Why is zinc not regarded as a transition element? (Atomic number Zn = 30)

ISC 2018

Ans :

Zinc with electronic configuration $[Ar]3d^{10}4s^2$ has completely filled shells of *d*-orbitals and therefore, it is not regarded as transition element. However, it is often studied with transition elements because of similarities in some of its properties to those of transition elements.

76. Why are the compounds of transition elements coloured ?

ISC 2021-22 (Sem-II), 2018

Ans :

Most of the complexes of transition elements are coloured. This is because of the absorption of radiation from visible light region to promote an electron from one of the *d*-orbitals to another. The ions of transition elements absorb the radiation of a particular wavelength and the rest is reflected, imparting colour to the solution.

77. What is the basic difference between the electronic configuration of transition and inner transition elements ?

ISC Specimen 2021-22 (Sem-II)

Ans :

The general electronic configuration of transition elements is $(n-1)d^{1-10}ns^{1-2}$ and for the inner transition elements the general electronic configuration is $(n-2)f^{1-14}(n-1)d^{0-1}ns^{0-2}$.

In transition metals elements, last electron enters in $(n-1)d$-orbitals. While in inner-transition elements, it enters in $(n-2)f$-orbitals.

78. Complete the following chemical reaction equations:

ISC 2017

(i) $MnO_4^-(aq) + C_2O_4^{2-}(aq) + H^+(aq) \longrightarrow$

(ii) $Cr_2O_7^{2-}(aq) + Fe^{2+}(aq) + H^+(aq) \longrightarrow$

Ans :

(i) $2MnO_4^-(aq) + 5C_2O_4^{2-}(aq) + 16H^+(aq) \longrightarrow 2Mn^{2+} + 8H_2O(l) + 10CO_2(g)$

(ii) $Cr_2O_7^{2-}(aq) + 6Fe^{2+}(aq) + 14H^+(aq) \longrightarrow 2Cr^{3+}(aq) + 6Fe^{3+}(aq) + 7H_2O(l)$

79. Give balanced equation when potassium iodide is treated with acidified potassium permanganate solution.

ISC 2024

Ans :

An acidified $KMnO_4$ solution oxidised potassium iodide to iodine.

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$$

$$[2KI + H_2SO_4 \longrightarrow K_2SO_4 + 2HI] \times 5$$
$$[2HI + O \longrightarrow H_2O + I_2] \times 5$$

$$2KMnO_4 + 8H_2SO_4 + 10KI \longrightarrow 6K_2SO_4 + 2MnSO_4 + 8H_2O + 5I_2$$

NODIA

80. Iron is ferromagnetic in nature. Explain why?

ISC 2011

Ans :

Ferro-magnetism is a special case of paramagnetism in which a substance acquires a permanent magnetic moment.

Paramagnetism is due to the presence of unpaired electrons in $(n-1)d$ orbital. As number of unpaired electrons increases, paramagnetism increases. Iron is much more paramagnetic than rest of the elements due to more number of unpaired electrons $[3d^6\ 4s^2]$and hence, it is termed as ferromagnetic. It is used to prepare permanent magnets.

81. State the common oxidation state of

(i) lanthanoids

(ii) actinoids

ISC 2025

Ans :

(i) In aqueous solution or in solid state, +3 state is more stable than other two oxidation states, i.e. +2 and + 4 in lanthanoid. This is due to sum of ionisation and lattice energies of their tripositive ion which is more negative than other two oxidation states.

(ii) The most common state for actinoids is +3. It is due to more negative value of sum of ionisation and lattice energy of their tripositive ion than other oxidation states.

82. Explain the following.

(i) Transition metals and their compounds generally exhibit a paramagnetic behaviour.

ISC 2020

(ii) There is an increase in density of elements from titanium $(Z=22)$ to copper $(Z=29)$ in the $3d$-series of transition elements.

ISC 2018

Ans :

(i) Transition metals have one or more unpaired electron. So, they readily occur paramagnetic nature.

(ii) While going from left to right in a period, the radii of transition elements remain similar but their atomic masses increases gradually. As a result, their density increases corresponding.

83. Why do the transition elements have higher enthalpies of atomisation? In $3d$ - series (Sc to Zn), which element has the lowest enthalpy of atomisation and why ?

ISC Specimen 2018

Ans :

The transition metals have high enthalpy of atomisation. It can be explained on the basis of strong inter-atomic interaction due to unpaired electrons. Greater the number of unpaired electrons, stronger is the resultant bonding. In $3d$-series Zn has the least enthalpy of atomisation because it has stable ground state configuration due to its completely filled d-orbital.

Thus, zinc has least tendency to form metallic bonds in the series.

84. In a given transition series, there is no significant changes in the atomic radii of elements with increase in atomic number. Explain why ?

ISC 2011

Ans :

Generally, atomic radii of transition elements belonging to a particular series decreases with increase in atomic number. As atomic number increases, the added electron enters in $(n-1)d$ subshell and thus, the shielding effect increases along with increase in nuclear charge.

However, the decrease in size with increase in nuclear charge due to increase in atomic number is counter balanced by the increased shielding effect of $(n-1)d$electrons. Hence, in a given transition series, there is no significant changes in the atomic radii of elements with increase in atomic number.

85. Why Zn^{2+} ions are colourless while Ni^{2+} ions are green and Cu^{2+} ions are blue in colour ?

ISC 2020

Ans :

Most of the compounds of transition metals are coloured both in solid state and in aqueous solution, due to d-d transition taking place between splitted d-orbitals of unpaired electron.

The transition meal ions having completely filled d-orbital (e.g. Zn^{2+}, Cu^{+}) and completely vacant d-orbitals are colourless (e.g. Sc^{3+}).

Zn^{+2} has completely filled d-orbitals

$(Zn^{+2}=[Ar]3d^{10}4s^{0})$ while Ni^{2+} has incomplete filled d-orbitals $Ni^{+2}=[Ar]3d^{8}4s^{0}$.

Thus, d-d transition takes place in Ni^{2+} and shows colour.

86. Give reason Zn^{2+} salts are white but Cu^{2+} salts are blue in colour.

ISC 2019, 2014, 2013, 2010

Ans :

The transition metal ions having completely filled d-orbitals or completely empty d-orbitals are colourless or white.

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Since, Zn^{2+} possesses completely filled *d*-orbitals as electronic configuration of Zn^{2+} is $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}$.

Thus, its salts are white or colourless. On the other hand, Cu^{2+} possesses an electronic configuration of $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^9$.

This suggest that it has partly filled *d*-orbitals (an unpaired e^-) which undergoes *d*-*d* transition. Hence, Cu^{2+} salts are coloured.

87. State a reason for each of the following.

ISC 2023

(i) $La(OH)_3$ is more basic than $Lu(OH)_3$.

(ii) Transition elements and their compounds act as catalyst.

Ans :

(i) $La(OH)_3$ is more basic than $Lu(OH)_3$ due to lanthanoid contraction. The size of lanthanoid ions decreases from La^{3+} to Lu^{3+}, the covalent character of the hydroxides increases and hence the basic strength decreases as we move from La^{3+} to Lu^{3+}

(ii) Most of the transition metals and their compounds act as a catalyst because of the variable oxidation states and the presence of vacant d-orbitals due to which they can form a variety of unstable intermediates. Further, large surface area of transition metals also attributes to their catalytic property.

88. Give reason for the following.

ISC Specimen 2023

(i) Transition metals form large number of complex compounds.

(ii) Transition elements show variable oxidation states.

Ans :

(i) Transition elements form a large number of complex compounds due to the comparatively smaller sizes of the metal ions, their high charge density and the availability of vacant *d*-orbitals for bond formation.

(ii) Transition elements show variable oxidation states in their compounds because there is a very small energy difference in between $(n-1)d$ and *ns*-orbitals.

As a result, electrons of $(n-1)d$-orbitals as well as *ns*-orbitals take part in bond formation.

NODIA

89. Explain why,

(i) transition elements form alloys ?

(ii) transition metals and their compounds act as catalyst ?

ISC 2019

Ans :

(i) The atomic radii of the transition elements in any series are not much different from each other. As a result, they can very easily replace each other in the lattice and form solid solutions over an appreciable composition range. Such solid solution are called alloys.

(ii) Many transition metals and their compounds are used as catalyst. This catalytic activity is due to their ability to adopt multiple oxidation states and to form complexes. Transition metals, because of their variable valencies sometimes form unstable intermediate compounds and provide a new path with lower activation energy for the reaction and thus, acts as a catalyst.

90. Explain why ?

ISC 2025

(i) Mn^{2+} is more stable than Fe^{2+} towards oxidation to + 3 state.
(Atomic number of Mn = 25, Fe = 26)

(ii) Zr and Hf exhibit similar properties.
(Atomic number of Zr = 40, Hf = 72)

Ans :

(i) Electronic configuration of Mn^{2+} is $3d^5$ which is half-filled and hence stable. Therefore, third ionisation enthalpy is very high, i.e. third electron cannot be lost easily. In case of Fe^{2+}, electronic configuration is $3d^6$. Hence, it can lose electron easily to give stable configuration, i.e. $3d^5$.

(ii) Due to lanthanoid contraction, Hf ($Z = 72$) has similar size to that of Zr ($Z = 40$). Hence, their properties are similar

91. Explain why transition metals form complex compound ?

ISC 2024

Ans :

Transition metal form a large number of complex compounds due to the following reasons.

(i) Small size.

(ii) High nuclear charge.

(iii) Availability of vacant d-orbitals of suitable energy for accommodating the lone pair of electrons donated by the ligands.

Due to small size of transition metal atoms or their cations and high effective nuclear charge, they have a high positive charge density on them. This high positive charged density makes the atoms or cation to attract the lone pair of electrons from the ligand and transition metal cation or atoms have vacant d-orbital in which they can accommodate the lone pair of electrons donated by ligands and thus, can form $L \rightarrow M$ coordinate bonds.

92. Give the balanced equation for acidified potassium permanganate and oxalic acid.

ISC 2012

Ans :

Thus, first write the balanced reduction and oxidation half reaction for $KMnO_4$ and oxalic acid respectively.

Then, write the overall balanced redox reaction. $KMnO_4$ oxidises oxalic acid (or oxalates) to carbon dioxide.

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$$

$$\left[\begin{matrix}COOH\\|\\COOH\end{matrix} + O \longrightarrow 2CO_2 + H_2O\right] \times 5$$

$$2KMnO_4 + 3H_2SO_4 + 5\begin{matrix}COOH\\|\\COOH\end{matrix} \longrightarrow$$

Oxalic acid

$$K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$$

93. Give a reason for the following.

ISC 2023

(i) Cu^{+2} salts are paramagnetic while Cu^{+} salts are diamagnetic.

(ii) Mn^{+2} compounds are more stable than Fe^{+2} compounds.

Ans :

(i) The electronic configuration of

$$Cu^{+} = 1s^2,\ 2s^2,\ 2p^6,\ 3s^2,\ 3p^6,\ 4s^0,\ 3d^{10}$$

and $Cu^{2+} = 1s^2,\ 2s^2,\ 2p^6,\ 3s^2,\ 3p^6,\ 4s^0,\ 3d^9$

In Cu^{+} ion, all electrons are paired. Hence, Cu^{+} is diamagnetic in nature. Whereas, Cu^{2+} has one unpaired electron thus, shows paramagnetic character.

(ii) Magnesium in +2 oxidation state form stable compounds than iron in +2 oxidation state.

$$Mn^{2+} = 1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^5$$

(half-filled d-orbital)

$$Fe^{2+} = 1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^6$$

Mn^{2+} compounds are more stable due to half-filled d-orbitals. Fe^{2+} compounds are comparatively less stable as they have six electrons in their $3d$-orbitals.

94. Explain the following :

(i) Why do transition metal ions posses a great tendency to form complexes ?

(ii) The paramagnetic character in $3d$ - transition series elements increases upto Mn and then decreases.

ISC 2015

Ans :

(i) Due to small size of transition metal atoms or their cations and high effective nuclear charge, they have a high positive charge density on them. This high positive charged density makes the atoms or cation to attract the lone pair of electrons from the ligand and transition metal cation or atoms have vacant d-orbital in which they can accommodate the lone pair of electrons donated by ligands and thus, can form $L \rightarrow M$ coordinate bonds.

(ii) Paramagnetic character increases with the increase in the number of unpaired electrons. The larger is the number of unpaired electron in central atom or ion greater is the paramagnetic character hence on moving from Sc to Mn, number of unpaired electron increases and then from Fe to Zn decreases. Thus, paramagnetic character also increases from Sc to Mn and then decreases from Fe to Zn.

95. Complete and balance the following chemical equations.

ISC Specimen 2023

(i) $KMnO_4 + H_2SO_4 + FeSO_4 \longrightarrow \_\_\_\_ + \_\_\_\_ + \_\_\_ + \_\_\_$

(ii) $K_2Cr_2O_7 + KI + H_2SO_4 \longrightarrow \_\_\_\_ + \_\_\_\_ + \_\_\_ + \_\_\_$

Ans :

(i) The given reaction takes place in acidic medium in which the ferrous salt is converted to ferric salt.

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 \quad 3H_2O + 5O$$

$$\left[2FeSO_4 + H_2SO_4 + O \longrightarrow Fe_2(SO_4)_3 + H_2O\right] \times 5$$

$$2KMnO_4 + 8H_2SO_4 + 10FeSO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$$

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(ii) In acidic medium $Cr_2O_7^{2-}$ is converted to Cr^{3+} and I^- is converted to I_2.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$
$$6I^- \longrightarrow 3I_2 + 6e^-$$
$$Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 2Cr^{3+} + 7H_2O + 3I_2$$

THREE MARKS QUESTIONS

96. Complete the following chemical equations.

ISC Specimen 2018

(i) $K_2Cr_2O_7 + H_2SO_4 + FeSO_4 \longrightarrow$

(ii) $K_2Cr_2O_7 + H_2SO_4 + H_2S \longrightarrow$

(iii) $KMnO_4 + H_2SO_4 + H_2C_2O_4 \longrightarrow$

Ans :

(i) $K_2Cr_2O_7 + 7H_2SO_4 + 6FeSO_4 \longrightarrow$
$K_2SO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O$

(ii) $K_2Cr_2O_7 + 4H_2SO_4 + 3H_2S \longrightarrow$
$K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3S$

(iii) $2KMnO_4 + 3H_2SO_4 + 5C_2H_2O_4 \longrightarrow$
$K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$

97. Complete and balance the following chemical equations.

ISC 2024, 2019

(i) $KMnO_4 + H_2SO_4 + H_2C_2O_4 \longrightarrow$
$\_\_\_\_ + \_\_\_\_ + \_\_\_ + \_\_\_$

(ii) $K_2Cr_2O_7 + H_2SO_4 + KI \longrightarrow$
$\_\_\_\_ + \_\_\_\_ + \_\_\_$

(iii) $K_2Cr_2O_7 + H_2SO_4 + FeSO_4 \longrightarrow$
$\_\_\_\_ + \_\_\_\_ + \_\_\_ + \_\_\_$

Ans :

(i) $2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 \xrightarrow{60^\circ C}$
$2MnSO_4 + 10CO_2 + K_2SO_4 + 8H_2O$

(ii) $K_2Cr_2O_7 + 6KI + 7H_2SO_4 \longrightarrow$
$3I_2 + Cr_2(SO_4)_3 + 4K_2SO_4 + 7H_2O$

(iii) $K_2Cr_2O_7 + 7H_2SO_4 + 6FeSO_4 \longrightarrow$
$3Fe_2(SO_4)_3 + K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O$

98. Complete and balance the following chemical equations.

ISC 2018

(i) $KMnO_4 + KI + H_2SO_4 \longrightarrow$
$\_\_\_\_ + \_\_\_\_ + \_\_ + \_\_\_$

(ii) $K_2Cr_2O_7 + H_2SO_4 + H_2S \longrightarrow$
$\_\_\_\_ + \_\_\_\_ + \_\_\_\_ + \_\_\_$

(iii) $KMnO_4 + H_2SO_4 + FeSO_4 \longrightarrow$
$\_\_\_\_ + \_\_\_\_ + \_\_\_ + \_\_\_$

Ans :

(i) $2KMnO_4 + 10KI + 3H_2SO_4 \longrightarrow$
$K_2SO_4 + 2MnSO_4 + 8H_2O + 5I_2$

(ii) $K_2Cr_2O_7 + 4H_2SO_4 + 3H_2S \longrightarrow$
$K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3S$

(iii) $2KMnO_4 + 8H_2SO_4 + 10FeSO_4 \longrightarrow$
$K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$

99. Account for the following. Explain why ?

ISC Specimen 2018

(i) Transition metals exhibit variable oxidation states.

(ii) Zr $(Z = 40)$ and Hf $(Z = 72)$ have almost identical radii.

(iii) Transition metals and their compounds act as a catalyst.

Ans :

(i) Transition metal exhibit variable oxidation states. This is because of the fact that the difference in the energy of $(n-1)d$-electrons and ns-electrons is low which implies that electrons from both energy levels can take part in bonding.

(ii) In lanthanoid due to poor shielding effect of $4f$-electrons the attraction between the electrons and the nucleus increases and hence atomic radius decreases. This is called lanthanoid contraction. Because of this reason Zr and Hf have almost identical radii.

(iii) Many transition metals and their compounds are used as catalyst. Their catalytic activity is due to their ability to adopt multiple oxidation states and to form complexes.

100. Compare the chemistry of the actinoids with that of lanthanoids with reference to the following :

ISC 2025

(i) Electronic configuration

(ii) Oxidation states

(iii) Chemical reactivity

Ans :

(i) **Electronic configuration :**

$$\text{Lanthanoids} = [Xe]4f^{0-14}\,5d^{0-1}\,6s^2$$
$$\text{Actinoids} = [Rn]5f^{0-14}6d^{0-1}7s^2$$

(ii) **Oxidation states** : In lanthanoids, +3 oxidation state is most common alongwith + 2 and + 4. While in actinoids, there is a

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greater range of oxidation states because $5f$, $6d$ and $7s$ levels are of comparable energies. They show +2, +3, +4, + 5, + 6 and +7 oxidation states. Common oxidation state in actinoids is + 3.

(iii) **Chemical reactivity** Lanthanoids are less reactive than actinoids. Actually, earlier members of lanthanoids are quite reactive similar to calcium but with increasing atomic number, they behave more like aluminium. Lanthanoids react with dilute acids to liberate 112 gas while actinoids react with boiling water and gives a mixture of oxide and hydride.

101. How does potassium dichromate prepared from a sample of chromite ore? Give the balanced equations for the chemical reactions involved.

ISC 2014

Ans :

Potassium di-chromate is generally manufactured from chromite ore $FeO \cdot Cr_2O_3$ or $FeCr_2O_4$.

The steps involved are

(i) Finely powdered chromite ore is mixed with Na_2CO_3 and quicklime. The mixture is roasted in a reverberatory furnace in the presence of excess of air. On account of roasting, a yellow mass containing sodium chromate is obtained.

$$4FeCr_2O_4 + O_2 \longrightarrow 2FeO_3 + 4Cr_2O_3$$

$$4Cr_2O_3 + 8Na_2CO_3 + 6O_2 \longrightarrow 8Na_2CrO_4 + 8CO_2$$

$$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \longrightarrow 2Fe_2O_3 + 8Na_2CrO_4 + 8CO_2$$

(ii) Sodium chromate obtained is treated with concentrated sulphuric acid where it is converted into sodium dichromate.

$$2Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

The solution is concentrated when less soluble sodium sulphate $Na_2SO_4 \cdot 10H_2O$ crystallises out. This solution is filtered hot. The solution is now cooled till sodium dichromate crystals $(Na_2Cr_2O_7 \cdot 2H_2O)$ separates out.

(iii) Hot concentrated solution of sodium dichromate is treated with calculated amount of potassium chloride and the mixture is cooled till orange crystals of potassium dichromate are obtained.

$$\underset{\text{(Hot and Conc.)}}{Na_2Cr_2O_7} + 2KCl \longrightarrow \underset{\text{(Orange)}}{K_2Cr_2O_7} + 2NaCl$$

FOUR MARKS QUESTIONS

102. Explain why $KMnO_4$ acts as a powerful oxidising agent in acidic medium.

ISC 2025

Ans :

In $KMnO_4$, manganese exists in +7 oxidation state, which is highly unstable.

In acidic medium, MnO_4^- ions readily gain electrons and get reduced to Mn^{2+} ions.

This reduction involves large decrease in oxidation state and therefore high oxidising power.

Hence potassium permanganate acts as a powerful oxidising agent in acidic medium.

103. Explain why transition elements generally possess high melting and boiling points.

ISC 2024

Ans :

Transition elements contain several unpaired d-electrons that participate in metallic bonding.

Strong overlap between d-orbitals and metallic lattice formation produce strong interatomic attraction.

Consequently large amount of energy is required to separate the atoms, resulting in high melting and boiling points compared to s-block elements.

104. Explain why transition metals readily form alloys and interstitial compounds.

ISC 2009

Ans :

Transition metals form alloys because they possess similar atomic sizes and crystal structures. Therefore atoms of one metal can replace atoms of another metal in metallic lattice easily.

They form interstitial compounds because small atoms like H, C and N can occupy vacant spaces in their crystal lattices.

These compounds are generally hard and possess high melting points.

105. Explain the structure of dichromate ion.

ISC 2017

Ans :

The dichromate ion consists of two tetrahedral CrO_4 units sharing one oxygen atom.

Each chromium atom is surrounded tetrahedrally by four oxygen atoms.

The two tetrahedra are linked through a bridging oxygen atom.

NODIA

Chromium atoms in dichromate ion undergo sp^3 hybridisation and the ion possesses characteristic orange colour.

106. Explain why transition elements generally show variable oxidation states. Illustrate your answer using manganese.

ISC 2013

Ans :

Transition elements possess ns and (n–1)d orbitals having nearly comparable energies. Therefore electrons from both orbitals can participate in bond formation.

As a result, transition elements exhibit a wide variety of oxidation states.

For example, manganese has electronic configuration $3d^5 4s^2$ and can show oxidation states from +2 to +7 because different numbers of 3d and 4s electrons participate in bonding.

107. Explain the origin of colour in transition metal compounds. Why are Zn^{2+} ions colourless?

ISC 2024

Ans :

Most transition metal ions possess partially filled d-orbitals. In presence of ligands, d-orbitals split into different energy levels.

Electrons absorb visible light and undergo d–d electronic transitions between these levels. The transmitted or reflected light gives characteristic colour to the compound.

Zn^{2+} ions possess completely filled $3d^{10}$ configuration and therefore d–d transitions are not possible, making Zn^{2+} ions colourless.

108. Explain the catalytic properties of transition elements.

ISC 2011

Ans :

Transition elements and their compounds act as good catalysts because of the following reasons:

(i) They possess variable oxidation states and can form unstable intermediate compounds with reactants.

(ii) They provide alternative reaction pathways having lower activation energy.

(iii) Finely divided transition metals provide large surface area for adsorption of reactant molecules.

Due to these factors, transition metals effectively increase the rate of chemical reactions.

109. Explain the magnetic behaviour of transition elements on the basis of electronic configuration.

ISC 2008

Ans :

Transition metal ions generally possess unpaired electrons in d-orbitals.

Presence of unpaired electrons causes paramagnetism because these electrons align in the direction of external magnetic field.

Greater the number of unpaired electrons, stronger is the paramagnetic behaviour.

Transition metal ions having completely filled d-orbitals do not contain unpaired electrons and therefore show diamagnetic behaviour.

110. Explain lanthanoid contraction and discuss its important consequences.

ISC 2007

Ans :

Lanthanoid contraction refers to the gradual decrease in atomic and ionic radii across the lanthanoid series from La to Lu.

It occurs because f-electrons provide poor shielding effect against increasing nuclear charge.

Consequences:

(i) Lanthanoids show very similar chemical properties and become difficult to separate.

(ii) Elements of second and third transition series exhibit similar atomic sizes and properties.

(iii) Basic strength of lanthanoid hydroxides decreases across the series.

111. Describe the preparation of potassium dichromate from chromite ore.

ISC 2001

Ans :

Chromite ore ($FeCr_2O_4$) is fused with sodium carbonate in presence of air to form sodium chromate.

The sodium chromate solution is acidified to convert chromate ions into sodium dichromate.

Sodium dichromate is then treated with KCl solution to obtain potassium dichromate crystals due to lower solubility of $K_2Cr_2O_7$.

Thus potassium dichromate is prepared industrially from chromite ore.

112. Explain the oxidising action of potassium dichromate in acidic medium with suitable reactions.

ISC 2021

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Ans :

Potassium dichromate acts as a strong oxidising agent in acidic medium because Cr^{6+} ions readily get reduced to Cr^{3+} ions.

Examples:

(i) Fe^{2+} is oxidised to Fe^{3+}

(ii) I^- ions are oxidised to I_2

(iii) SO_2 is oxidised to H_2SO_4

During these reactions, dichromate ions gain electrons and undergo reduction, while the other substances are oxidised.

113. Compare lanthanoids and actinoids on the basis of oxidation states, radioactivity and bonding behaviour.

ISC 2023

Ans :

Lanthanoids	**Actinoids**
Most common oxidation state is +3	Show wider range of oxidation states
Generally non-radioactive except promethium	All actinoids are radioactive
Bonding mainly ionic	Bonding shows greater covalent character
4f orbitals participate weakly in bonding	5f orbitals participate more effectively

Thus actinoids show more complex chemistry than lanthanoids.

114. Explain why actinoids show greater range of oxidation states than lanthanoids.

ISC 2002

Ans :

In actinoids, 5f, 6d and 7s orbitals possess nearly comparable energies.

Therefore electrons from all these orbitals can participate in bonding.

As different numbers of electrons may be involved in bond formation, actinoids exhibit wide variety of oxidation states ranging from +3 to +6 or higher.

Lanthanoids mainly show +3 oxidation state because 4f orbitals participate less effectively.

115. Explain the role of transition metals in formation of coloured complexes.

ISC 2005

Ans :

Transition metal ions possess partially filled d-orbitals. When ligands approach the metal ion, d-orbitals split into different energy levels due to crystal field effect.

Electrons absorb visible light and undergo d–d transitions between split orbitals.

The absorbed wavelength determines the complementary colour observed in the coordination complex.

Hence most transition metal complexes are coloured.

116. Explain the reasons for the following properties of transition elements:

ISC 2017

(i) High density

(ii) Formation of complexes

(iii) Paramagnetic behaviour

(iv) Alloy formation

Ans :

(i) Transition metals possess high atomic masses and comparatively small atomic radii, resulting in high densities.

(ii) They form complexes because of small ionic size, high nuclear charge and vacant d-orbitals.

(iii) Paramagnetism arises due to presence of unpaired electrons in d-orbitals.

(iv) They form alloys because their atomic sizes are very similar and atoms can substitute one another in metallic lattice easily.

NUMERICAL QUESTIONS

117. Calculate the oxidation state of chromium in CrO_4^{2-} ion.

ISC 2004

Ans :

Let oxidation state of chromium $= x$

$$x + 4(-2) = -2$$

$$x - 8 = -2$$

$$x = +6$$

Therefore, oxidation state of chromium is $+6$.

NODIA

118. Calculate the oxidation state of manganese in MnO_2.

ISC 2024

Ans :

Let oxidation state of manganese $= x$

$$x + 2(-2) = 0$$
$$x - 4 = 0$$
$$x = +4$$

Therefore, oxidation state of manganese is $+4$.

119. Calculate the oxidation state of manganese in MnO_4^- ion.

ISC 2003

Ans :

Let oxidation state of manganese $= x$

$$x + 4(-2) = -1$$
$$x - 8 = -1$$
$$x = +7$$

Therefore, oxidation state of manganese is $+7$.

120. Calculate the oxidation state of manganese in $KMnO_4$.

ISC 2022

Ans :

Let oxidation state of manganese $= x$

$$(+1) + x + 4(-2) = 0$$
$$1 + x - 8 = 0$$
$$x = +7$$

Therefore, oxidation state of manganese is $+7$.

121. Calculate the oxidation state of chromium in $K_2Cr_2O_7$.

ISC 2017

Ans :

Let oxidation state of chromium $= x$

$$2(+1) + 2x + 7(-2) = 0$$
$$2 + 2x - 14 = 0$$
$$2x = 12$$
$$x = +6$$

Therefore, oxidation state of chromium is $+6$.

122. A transition metal ion contains three unpaired electrons. Calculate its magnetic moment.

ISC 2024

Ans :

Using formula:

content":" $\mu = \sqrt{n(n+2)}$ BM

For $n = 3$

$$\mu = \sqrt{3(3+2)}$$
$$= \sqrt{15}$$
$$= 3.87 \text{ BM}$$

Therefore, the magnetic moment is 3.87 BM.

123. The magnetic moment of a transition metal ion is 1.73 BM. Determine the number of unpaired electrons present in the ion.

ISC 2000

Ans :

$$\mu = \sqrt{n(n+2)}$$
$$1.73 = \sqrt{3}$$
$$n(n+2) = 3$$
$$n^2 + 2n - 3 = 0$$
$$n = 1$$

Therefore, the ion contains 1 unpaired electron.

124. Calculate the magnetic moment of Ni^{2+} ion having two unpaired electrons.

ISC 2007

Ans :

Using formula:

$$\mu = \sqrt{n(n+2)} \text{ BM}$$

For $n = 2$

$$\mu = \sqrt{2(2+2)}$$
$$= \sqrt{8}$$
$$= 2.83 \text{ BM}$$

Therefore, the magnetic moment is 2.83 BM.

125. A transition metal ion has magnetic moment 5.92 BM. Calculate the number of unpaired electrons present.

ISC 2020

Ans :

$$\mu = \sqrt{n(n+2)}$$
$$5.92 = \sqrt{35}$$
$$n(n+2) = 35$$
$$n^2 + 2n - 35 = 0$$
$$n = 5$$

Therefore, the ion contains 5 unpaired electrons.

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126. Calculate the magnetic moment of Co^{2+} ion having three unpaired electrons.

ISC 2019

Ans :

Using formula:

$$\mu = \sqrt{n(n+2)}\ \text{BM}$$

For $n = 3$

$$\mu = \sqrt{3(3+2)}$$
$$= \sqrt{15}$$
$$= 3.87\ \text{BM}$$

Therefore, the magnetic moment is 3.87 BM.

127. Calculate the oxidation state of chromium in $Cr_2O_7^{2-}$ ion.

ISC 2008

Ans :

Let oxidation state of chromium $= x$

$$2x + 7(-2) = -2$$
$$2x - 14 = -2$$
$$2x = 12$$
$$x = +6$$

Therefore, oxidation state of chromium is $+6$.

128. A transition metal ion possesses four unpaired electrons. Calculate its magnetic moment

ISC 2010

Ans :

Using formula:

$$\mu = \sqrt{n(n+2)}\ \text{BM}$$

For $n = 4$

$$\mu = \sqrt{4(4+2)} = \sqrt{24}$$
$$= 4.90\ \text{BM}$$

Therefore, the magnetic moment is 4.90 BM.

129. Calculate the oxidation state of manganese in Mn_2O_7.

ISC 2021

Ans :

Let oxidation state of manganese $= x$

$$2x + 7(-2) = 0$$
$$2x - 14 = 0$$
$$2x = 14$$
$$x = +7$$

Therefore, oxidation state of manganese is $+7$.

130. Calculate the magnetic moment of a transition metal ion having one unpaired electron.

ISC 2009

Ans :

Using formula:

$$\mu = \sqrt{n(n+2)}\ \text{BM}$$

For $n = 1$

$$\mu = \sqrt{1(1+2)}$$
$$= \sqrt{3}$$
$$= 1.73\ \text{BM}$$

Therefore, the magnetic moment is 1.73 BM.

131. Determine the number of unpaired electrons in a metal ion having magnetic moment 3.87 BM.

ISC 2001

Ans :

$$\mu = \sqrt{n(n+2)}$$
$$3.87 = \sqrt{15}$$
$$n(n+2) = 15$$
$$n^2 + 2n - 15 = 0$$
$$n = 3$$

Therefore, the ion contains 3 unpaired electrons.

132. A transition metal ion contains two unpaired electrons. Calculate its magnetic moment.

ISC 2017

Ans :

Using formula:

$$\mu = \sqrt{n(n+2)}\ \text{BM}$$

For $n = 2$

$$\mu = \sqrt{2(2+2)} = \sqrt{8}$$
$$= 2.83\ \text{BM}$$

Therefore, the magnetic moment is 2.83 BM.

133. Calculate the oxidation state of chromium in Cr_2O_3.

ISC 2021

Ans :

Let oxidation state of chromium $= x$

$$2x + 3(-2) = 0$$
$$2x - 6 = 0$$
$$2x = 6$$
$$x = +3$$

Therefore, oxidation state of chromium is $+3$.

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134. The magnetic moment of a transition metal ion is found to be 4.90 BM. Calculate the number of unpaired electrons present in the ion.

ISC 2012

Ans :

Using formula:

$$\mu = \sqrt{n(n+2)}\ \text{BM}$$

$$4.90 = \sqrt{n(n+2)}$$

Squaring both sides:

$$24 = n(n+2)$$

$$n^2 + 2n - 24 = 0$$

$$n = 4$$

Therefore, the ion contains 4 unpaired electrons.

135. The magnetic moment of a transition metal ion is 2.83 BM. Determine the number of unpaired electrons present.

ISC 2025

Ans :

$$\mu = \sqrt{n(n+2)}$$

$$2.83 = \sqrt{8}$$

$$n(n+2) = 8$$

$$n^2 + 2n - 8 = 0$$

$$n = 2$$

Therefore, the ion contains 2 unpaired electrons.

136. Calculate the magnetic moment of Fe^{3+} ion having five unpaired electrons.

ISC 2021

Ans :

Using formula:

$$\mu = \sqrt{n(n+2)}\ \text{BM}$$

For $n = 5$

$$\mu = \sqrt{5(5+2)}$$

$$= \sqrt{35}$$

$$= 5.92\ \text{BM}$$

Therefore, the magnetic moment of Fe^{3+} ion is 5.92 BM.

CASE BASED QUEATIONS

137. A student prepared aqueous solutions of $CuSO_4$ and $ZnSO_4$ in separate test tubes. He observed that $CuSO_4$ solution was blue whereas $ZnSO_4$ solution was colourless. His teacher explained the observation on the basis of electronic configuration and d–d transitions.

(i) Why is $CuSO_4$ solution coloured?
(ii) Why is $ZnSO_4$ solution colourless?
(iii) Explain the role of d–d transition in producing colour in transition metal ions.

Ans :

(i) Cu^{2+} ions possess partially filled d-orbitals and therefore appear coloured.
(ii) Zn^{2+} ions possess completely filled $3d^{10}$ configuration and are colourless.
(iii) In transition metal ions, d-orbitals split into different energy levels in presence of ligands. Electrons absorb visible light and undergo d–d transitions between these levels, producing characteristic colours in transition metal compounds.

138. A student compared the magnetic behaviour of Fe^{2+} and Zn^{2+} ions using a magnetic field. Fe^{2+} ions were attracted strongly towards the magnetic field whereas Zn^{2+} ions were not attracted.

(i) Which ion is paramagnetic?
(ii) Why are Zn^{2+} ions diamagnetic?
(iii) Explain the relationship between unpaired electrons and magnetic behaviour of transition metal ions.

Ans :

(i) Fe^{2+} ions are paramagnetic.
(ii) Zn^{2+} ions possess no unpaired electrons.
(iii) Paramagnetism arises due to presence of unpaired electrons in atomic orbitals. Greater the number of unpaired electrons, stronger is the attraction towards magnetic field. Transition metal ions with all electrons paired show diamagnetic behaviour.

139. During a laboratory experiment, potassium dichromate was used to oxidise Fe^{2+} ions in acidic medium. The orange colour of dichromate solution gradually changed to green.

(i) Which ion is responsible for the green colour formed during the reaction?
(ii) Why is potassium dichromate used in acidic medium?

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(iii) Explain the oxidising behaviour of potassium dichromate in acidic medium.

Ans :

(i) Cr^{3+} ions are responsible for the green colour.

(ii) Potassium dichromate acts as a strong oxidising agent in acidic medium.

(iii) In acidic medium, $Cr_2O_7^{2-}$ ions readily gain electrons and get reduced from Cr^{6+} to Cr^{3+}. This strong tendency to undergo reduction enables potassium dichromate to oxidise Fe^{2+} ions and other reducing agents effectively.

140. A chemistry student studied the properties of $KMnO_4$ in acidic and alkaline medium. He observed that $KMnO_4$ showed much stronger oxidising behaviour in acidic medium.

(i) What is the oxidation state of manganese in $KMnO_4$?

(ii) To which oxidation state is Mn reduced in acidic medium?

(iii) Explain why $KMnO_4$ acts as a stronger oxidising agent in acidic medium.

Ans :

(i) The oxidation state of manganese in $KMnO_4$ is +7.

(ii) Mn is reduced to +2 oxidation state.

(iii) In acidic medium, MnO_4^- ions readily gain electrons and undergo reduction from +7 to +2 oxidation state. This large decrease in oxidation state results in high oxidising power of potassium permanganate.

141. A student observed that transition metals such as iron, nickel and chromium form several industrial alloys. Stainless steel was discussed as an important example.

(i) Why do transition metals readily form alloys?

(ii) Name one important alloy containing chromium.

(iii) Explain the importance of chromium in stainless steel.

Ans :

(i) Because transition metals possess similar atomic sizes and crystal structures.

(ii) Stainless steel.

(iii) Chromium forms a thin protective oxide layer on the surface of steel. This layer prevents corrosion and rusting, thereby increasing strength, durability and resistance towards chemical attack in stainless steel.

142. A student observed gradual decrease in ionic radii from La^{3+} to Lu^{3+} while studying lanthanoids. The teacher related this observation to shielding effect of electrons.

(i) What is this gradual decrease in ionic radii called?

(ii) Which electrons are mainly responsible for this effect?

(iii) Explain why lanthanoid contraction occurs.

Ans :

(i) It is called lanthanoid contraction.

(ii) f-electrons are mainly responsible.

(iii) f-electrons provide poor shielding effect against increasing nuclear charge. Consequently effective nuclear attraction increases across the lanthanoid series, causing gradual decrease in atomic and ionic radii.

143. During a practical demonstration, a finely divided nickel catalyst was used in hydrogenation of vegetable oils. The reaction proceeded rapidly compared to reaction without catalyst.

(i) Which property of transition metals enables catalytic activity?

(ii) Why is finely divided nickel preferred over nickel lumps?

(iii) Explain the catalytic action of transition metals.

Ans :

(i) Ability to form unstable intermediate compounds.

(ii) Finely divided nickel provides larger surface area for adsorption.

(iii) Transition metals form unstable intermediates with reactants and provide alternative pathways of lower activation energy. Finely divided metals also increase adsorption of reactants, increasing reaction rate significantly.

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144. A student compared lanthanoids and actinoids and observed that actinoids show greater variation in oxidation states than lanthanoids.

(i) Which orbitals participate in bonding in actinoids?

(ii) What is the most common oxidation state of lanthanoids?

(iii) Explain why actinoids show greater range of oxidation states.

Ans :

(i) 5f, 6d and 7s orbitals participate in bonding.

(ii) The most common oxidation state is +3.

(iii) The energies of 5f, 6d and 7s orbitals are nearly comparable in actinoids. Therefore different numbers of electrons can participate in bonding, producing wide range of oxidation states.

145. A transition metal compound was found to exhibit strong paramagnetic behaviour and deep colour in aqueous solution. The student concluded that the ion contains partially filled d-orbitals.

(i) Which type of electrons are responsible for paramagnetism?

(ii) Which phenomenon produces colour in transition metal ions?

(iii) Explain why partially filled d-orbitals are important in transition element chemistry.

Ans :

(i) Unpaired electrons are responsible for paramagnetism.

(ii) d–d electronic transitions produce colour.

(iii) Partially filled d-orbitals enable transition elements to exhibit colour, paramagnetism, variable oxidation states and complex formation. These unique properties distinguish transition elements from normal metallic elements.

146. A student studied interstitial compounds formed by transition metals with carbon and nitrogen. He observed that these compounds were extremely hard and possessed high melting points.

(i) What are interstitial compounds?

(ii) Which small atoms commonly occupy interstitial spaces?

(iii) Explain why interstitial compounds are generally hard and possess high melting points.

Ans :

(i) Interstitial compounds are compounds in which small atoms occupy spaces in metallic crystal lattice.

(ii) Hydrogen, carbon and nitrogen atoms commonly occupy interstitial spaces.

(iii) Small atoms present in interstitial spaces strengthen the metallic lattice and increase interatomic attraction. Consequently interstitial compounds become hard and possess high melting points and rigidity.

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CHAPTER 5

Coordination Compounds

SUMMARY

1. ADDITION COMPOUND

When two or more stable compound combine together in stoichiometric ratio then the compound formed is called addition compound .It is of following types

1.1 Coordination Compounds or Complex Compounds

Those compounds in which the central metal atom is linked to ions or neutral molecules by coordinate bond are called coordinate compounds or complex e.g. $K_4[Fe(CN)_6]$.

Complex Ion

Ion formed by coordinate bond between central metal atom and donor is called complex ion.

There are three types of complexes:

1. Cationic complex e.g., $[Co(NH_3)_6]^{3+}$
2. Anionic complex e.g., $[Ag(CN)_2]^-$
3. Neutral complex e.g., $[Ni(CO)_4]$.

1.2 Double Salts

These salt are formed by the combination of two simple salts in equimolar ratio. They lose then identity in the solution e.g., $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$.

$FeSO_4(NH_4)_2SO_4 \cdot 6H_2O \longrightarrow Fe^{2+} + 2NH_4^+ + 2SO_4^{2-} + 6H_2O$
(Mohr's salt)

Complex compound do not lose their identity in the solution.

$$K_4[Fe(CN)_6] \longrightarrow 4K^+ + [Fe(CN)_6]^{4-}$$

2. IMPORTANT TERMS USED IN COORDINATION CHEMISTRY

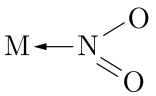
Some important terms related to the coordinate chemistry are given below :

1. **Ligand :** The donor species which donate a pair of electrons to the metal atom is called ligand.

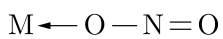
2. **Denticity :** The number of coordinating groups present in a ligand is called the denticity of the ligand.

   Based on denticity, ligands are classified as follows:

   1. **Monodentate ligand** : It have one donar atoms example NH_3, H_2O.
   2. **Bidentate ligand :** It can donate two lone pair of electrons example : en, ox.
   3. Hexadentate ligand : Hexadentate ligand has six donar atoms example $EDTA^{4-}$.
   4. Ambidentate Ligand : Unidentate ligands which have more than one coordination atoms are called ambidentate ligands example NO_2^-.



Nitrito-N



Nitrito-O

3. **Chelate :** When a bidentate or a polydentate ligand is attached by two or more donar atoms to the central atom forming a ring, the ligand is called chelate ligand and the complex is called chelate the effect is called chelate effect.

4. **Coordination Number :** Total number of coordinate bonds formed with the central metal atom or ion by the ligands.

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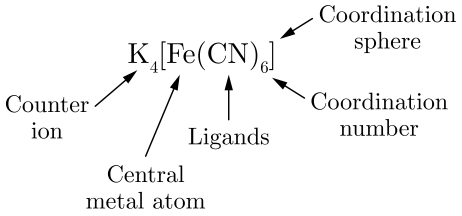
5. **Coordination Ion :** The ionizable group which are written outside the bracket are called counter ion.



6. **Oxidation Number :** Oxidation number or oxidation state of the central metal atom is calculated from the charge on the complex ion. $[Fe(CN)_6]^{4-}$

$$x + 6(-1) = -4$$
$$x = +2$$
$$\text{Oxidation state of Fe} = +2$$

3. NOMENCLATURE OF COORDINATION COMPOUNDS

The following rules are followed for naming of coordination compounds.

1. **Order of Naming Ions :** In a coordination compound, the cation is named first, followed by the anion, regardless of whether the cation or anion is the complex ion. This is the same convention followed in naming simple ionic compounds.
2. **Naming of Coordination Sphere :** Within the coordination sphere (the complex ion written inside square brackets), the ligands are named first in alphabetical order, followed by the name of the central metal ion. The oxidation state of the central metal ion is indicated by a Roman numeral in parentheses immediately after the name of the metal.
3. **Naming of Ligands :** Names of negative (anionic) ligands end in -o, names of neutral ligands retain their molecule names (e.g., aqua, ammine, carbonyl), and names of positive (cationic) ligands end in -ium..
4. **Order of Naming Ligands :** Ligands are named in alphabetical order.
5. **Numerical Prefixes :** To indicate the number of ligands of the same type prefix di, tri, tetra, penta or hexa is used when the name of complex ligand already has di, tri, etc. then the prefix used are bis, tris, tetrakis etc.
6. **Ending the Name of Metal Ion or Atom :** When the complex ion is anionic, the name of central metal atom ends in −ate and in cationic or neutral complexes the name of metal is written as such.
7. **Oxidation State of Central Metal Ion :** It is indicated by a Roman numeral and written after metal in brackets example.
   $K_4[Fe(CN)_6]$ potassium hexacyanoferrate (II)
   $[Co(NH_3)_6]Cl_3$ hexammine cobalt (III) chloride.

4. ISOMERISM IN COORDINATION COMPOUNDS

Compounds having the same molecular formula but differing in the arrangement of atoms or groups are called isomers, and the phenomenon is called isomerism. The following types of isomerism are exhibited by coordination compounds:

1. Ionisation Isomerism : The compounds which have the same molecular formula but give different ions in solution are called ionisation isomers, and this phenomenon is called ionisation isomerism.
   It arises when the counter ion (ion outside the coordination sphere) and a ligand (ion inside the coordination sphere) exchange their positions.
   Examples : $[Co(NH_3)_5Br]SO_4$, $[Co(NH_3)_5SO_4]Br$
2. Hydrate or Solute Isomerism : The compounds which have the same composition but differ in the number of water (solvent) molecules present as ligands inside the coordination sphere are called hydrate isomers. These isomers differ in their physical and chemical properties, such as colour and the number of water molecules released on heating.
   Examples : $[Cr(H_2O)_6]Cl_3$ $[Cr(H_2O)_5Cl]Cl \cdot H_2O$
3. Linkage Isomerism : It occurs in compounds which having ambidentate ligands showing different modes of attachment to metal through either of the two different donar atom.
   Example :
   $[Co(NH_3)_5(NO_2)]Cl_2$, $[Co(NH_3)(ONO)]Cl_2$
4. Coordination Isomerism : It arises when both the cation and anion are complexes which differ in the distribution of ligands.
   Example :
   $[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$

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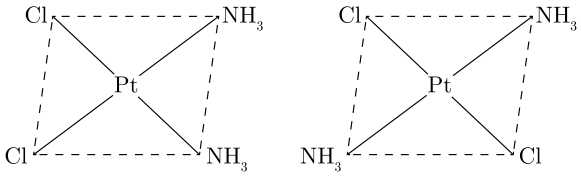
5. Geometrical Isomerism : This type of isomerism arises when ligands occupy different position around the central metal atom.
   1. **Cis-isomer :** When two identical ligands occupy adjacent position.
   2. **Trans-isomer :** When two identical ligands are opposite to each other.

   Example : $[Pt(NH_3)_2Cl_2]$

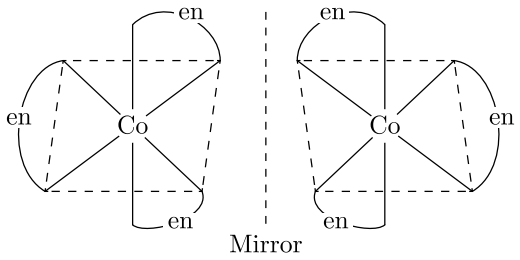


6. Optical Isomerism : Optical isomers rotate the plane polarised light in opposite direction i.e. right and left are called dextro (d) and laevo (l) isomers.

Enantiomers : The d and l isomers of a compounds are called enantiomers.

Chirality : The two isomers d and l are non-superimposable mirror image of each other are called chiral and this property is called chirality.

Optical Isomers : Optical isomers of $[CO(en)_3]^{3+}$



5. WERNER'S THEORY

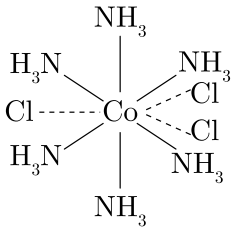
Alfred Werner (1866–1919), a Swiss chemist, proposed his theory of coordination compounds in 1893. He was awarded the Nobel Prize in Chemistry in 1913 for this work. The theory was the first successful attempt to explain the nature of bonding in complex compounds.

The main postulates are:

(i) Metals possess two types of valancies :
   (a) Primary or ionizable valency
   (b) secondary or non ionizable valency.

(ii) Every metal atom has a tendency to satisfy both its primary and secondary valancies.

(iii) The ligand satisfying secondary valencies are directional and give a definite geometry to the complex but primary valency are non directional.



Primary valencies are represented by dotted lines and secondary valencies by solid lines.

5.1 Limitations of Werner's theory:

(i) Why only certain elements form coordination compounds?

(ii) Why the coordination sphere has a definite geometry?

(iii) Why do coordination compounds possess definite magnetic and optical properties?

6. VALENCE BOND THEORY

1. Metal ligand bond is formed by the donation of pairs of electron by ligand to the metal atom.
2. Metal atom must possess vacant orbitals to accommodate these electrons. These orbitals are obtained by hybridisation.
3. Sometimes the unpaired (n-1) d electrons pair up prior to hybridization for making some (n-1) d orbitals vacant.
4. Metal-ligand bonds are formed by the overlap of these orbitals with ligand orbitals, these bonds are of equal strength and directional in nature.
5. Octahedral complexes are formed by d^2sp^3 or sp^3d^2 hybridisation. Square planar complexes are formed by dsp^2 hybridisation, tetrahedral complexes are formed by sp^3 hybridisation.
6. d^2sp^3 hybridized complex involve the inner (n-1) d orbitals these complexes are called inner orbital or low spin complexes.
   Examples : $[Co(NH_3)_6]^{3+}$, $[Fe(CN)_6]^{3-}$
7. sp^3d^2 hybridized complex involve the outer (nd) orbitals, these complexes are called outer orbital or high spin complexes. Example : $[Fe(H_2O)_6]^{3+}$, $[(CoF_6)]^{3-}$

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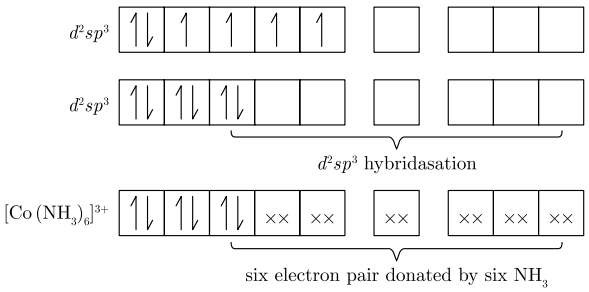
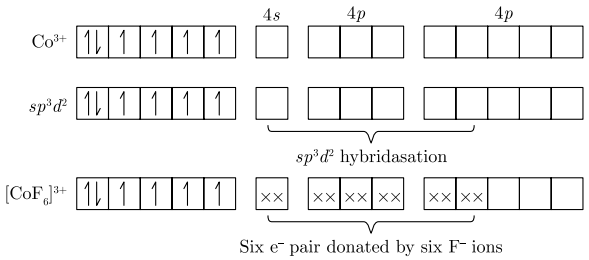
8. Formation of $[Co(NH_3)_6]^{3+}$



It is a diamagnetic complex due to absence of unpaired electron.

9. Formation of $[CoF_6]^{3-}$



It is strongly paramagnetic due to presence of five unpaired electrons.

6.1 Drawbacks of valence bond theory:

The drawbacks of valence bond theory are as follows :

1. It cannot explain why some complexes of a metal ion in a particular oxidation state are inner orbital complexes while some other complexes of the same metal ion in the some oxidation state are outer spin orbital complex.
2. It could not give any explanation for the colour of the complex.
3. It does not distinguish between weak and strong ligands.
4. It does not give a clear explanation of thermodynamic stabilities of coordination compounds.

7. CRYSTAL FIELD THEORY

Crystal Field Theory was proposed by Hans Bethe and John Van Vleck in 1929–1935. It is an electrostatic model that describes the effect of the ligand environment on the energy levels of the d-orbitals of a central metal ion in a coordination compound. The main postulates of crystal field theory are as follows:

1. Metal ligand bonds are ionic having electrostatic interaction, similar to ions in a crystal, therefore named as crystal field theory (CFT).
2. Ligand is treated as a point of negative charge. The arrangement of the ligands around the central ion is such that the repulsion between them are minimum.
3. In free transition metal ion all the five d-orbitals have equal energies i.e. they are degenerate. Due to ligand the degeneracy is split because those orbitals which have lobes along the axes towards ligands fell greater repulsion. The splitting of the degenerate level due to presence of ligand is called crystal field splitting.

7.1 Splitting of d-orbitals in Octahedral Crystal Field

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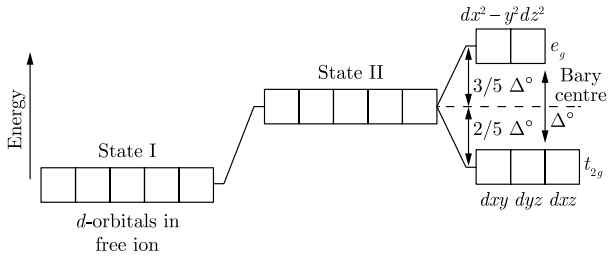

The difference of energy between the two sets of d-orbitals is called crystal field splitting energy or crystal field stabilization energy (CFSE). It is represented by Δ_0 for octahedral and Δ_t for tetrahedral

$$\Delta_t = \frac{4}{9}\Delta_0$$

8. SPECTROCHEMICAL SERIES

The arrangement of ligands in order of their increasing crystal field splitting energy (CFSE) are called spectrochemical series as given below:

$$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < edta^{4-} < NH_3 < en < CN^- < CO$$

9. IMPORTANCE OF COORDINATION COMPOUNDS

Coordination compounds are of great importance in several fields. The importance of coordination compounds is as follows:

produce large crystal field splitting energy, forcing electrons in lower energy orbitals to pair up. Consequently inner orbital low-spin complexes such as $[Ni(CN)_4]^{2-}$ are formed and often become diamagnetic.

11. A coordination compound exhibited optical isomerism despite having the same molecular formula and connectivity. The compounds are best described as:

ISC 2025

(a) Structural isomers

(b) Enantiomers

(c) Hydrate isomers

(d) Ionisation isomers

Ans : (b) Enantiomers

Optical isomers are non-superimposable mirror images of each other and rotate plane polarised light in opposite directions. Such isomers are called enantiomers. They possess identical physical properties except for their behaviour towards plane polarised light and chiral environments.

12. The complex $[Fe(CN)_6]^{4-}$ is diamagnetic because:

ISC 2020

(a) Iron possesses no d-electrons

(b) Cyanide ion is a strong field ligand causing electron pairing

(c) Iron exists in highest oxidation state

(d) Coordination number becomes zero

Ans : (b) Cyanide ion is a strong field ligand causing electron pairing

In $[Fe(CN)_6]^{4-}$, cyanide ions produce large crystal field splitting energy and force pairing of d-electrons in lower energy orbitals. As a result no unpaired electrons remain in the complex, making the complex diamagnetic according to crystal field theory and valence bond theory.

13. The complex $[Co(NH_3)_4Cl_2]^+$ exhibits geometrical isomerism because:

ISC 2011

(a) Ligands occupy different spatial positions around central metal ion

(b) The oxidation state of cobalt changes continuously

(c) Chloride ions are outside coordination sphere

(d) Ammonia behaves as ambidentate ligand

Ans : (a) Ligands occupy different spatial positions around central metal ion

Geometrical isomerism arises when identical ligands occupy different positions in space relative to one another around the central metal atom. In octahedral complexes like$[Co(NH_3)_4Cl_2]^+$, ligands may occupy adjacent cis positions or opposite trans positions, producing geometrical isomers.

14. According to Werner's theory, ligands satisfying secondary valencies are:

ISC 2004

(a) Ionisable and non-directional

(b) Non-ionisable and directional

(c) Always negatively charged only

(d) Responsible for metallic bonding only

Ans : (b) Non-ionisable and directional

Werner proposed that secondary valencies correspond to coordination number and are satisfied by ligands directly attached to the central metal atom. These valencies are non-ionisable and directional in nature, thereby determining the definite geometry and spatial arrangement of ligands around the metal ion.

15. The complex $[Fe(H_2O)_6]^{2+}$ is paramagnetic whereas $[Fe(CN)_6]^{4-}$ is diamagnetic. This difference mainly arises due to:

ISC 2009

(a) Difference in coordination number

(b) Difference in oxidation state of iron

(c) Difference in crystal field splitting caused by ligands

(d) Difference in molecular mass

Ans : (c) Difference in crystal field splitting caused by ligands

Water is a weak field ligand and produces small crystal field splitting, leaving unpaired electrons in the d-orbitals. Cyanide ion is a strong field ligand causing electron pairing due to large splitting energy. Consequently one complex becomes paramagnetic while the other becomes diamagnetic.

16. EDTA acts as a highly stable chelating ligand because it:

ISC 2011

(a) Possesses six donor atoms capable of coordinate bonding

(b) Contains only oxygen donor atoms

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5. The coordination number and oxidation state of the element '*E*' in the complex $[E(NH_3)_4Cl_2]NO_3$ are respectively.

ISC 2021-22 (Sem-II)

(a) 6 and 3 (b) 6 and 2

(c) 4 and 2 (d) 4 and 3

Ans : (a) 6 and 3

Coordination number: 4 NH_3 + 2 Cl^- = 6 ligands inside the bracket.

Oxidation state: NO_3^- is outside the coordination sphere (charge = -1). The complex ion carries a charge of +1 to balance NO_3^-.

$$E + 4(0) + 2(-1) = +1$$
$$E - 2 = +1$$
$$E = +3$$

6. In the complexes $[Fe(CN)_6]^{3-}$ and $[Pt(en)(H_2O)(NO_2)(Cl)]^{2+}$ the respective oxidation numbers of central metal atoms are

ISC 2018, 2015

(a) + 3 and + 4 (b) + 6 and + 4

(c) + 6 and + 3 (d) + 3 and + 3

Ans : (a) + 3 and + 4

$[Fe(CN)_6]^{3-}$

Let the oxidation number of Fe = x

$$x + 6 \times (-1) = -3$$
$$x = +3$$

$[Pt(en)(H_2O)_2(NO_2)(Cl)]^{2+}$

Let the oxidation number of Pt = x,

$$x + (0) + 2(0) + (-1) + (-1) = +2$$
$$x = +4$$

7. The complex ion $[Ni(CN)_4]^{2-}$ is

ISC 2017

(a) square planar and diamagnetic

(b) tetrahedral and paramagnetic

(c) square planar and paramagnetic

(d) tetrahedral and diamagnetic

Ans : (a) Square planar and diamagnetic.

Ni in $[Ni(CN)_4]^{2-}$: oxidation state = +2.

Electronic configuration of Ni^{2+} = [Ar] $3d^8$.

CN^- is a strong field ligand → causes pairing of electrons → all 8 electrons pair up in 3d orbitals, leaving one 3d orbital empty.

Hybridisation: dsp^2 (one inner 3d + one 4s + two 4p orbitals) → Square planar geometry.

Since all electrons are paired → no unpaired electrons → diamagnetic.

8. A student added excess $AgNO_3$ solution separately to aqueous solutions of $[Co(NH_3)_5Cl]SO_4$ and $[Co(NH_3)_5SO_4]Cl$. Different precipitates were obtained immediately. This observation confirms the existence of:

ISC 2008

(a) Geometrical isomerism

(b) Coordination isomerism

(c) Ionisation isomerism

(d) Optical isomerism

Ans : (c) Ionisation isomerism

Ionisation isomerism arises when a ligand inside the coordination sphere exchanges position with the counter ion outside the coordination sphere. Consequently different ions are produced in solution. Therefore the compounds give different precipitates with reagents like $AgNO_3$, confirming ionisation isomerism in coordination compounds.

9. The complex $[Co(NH_3)_6]Cl_3$ behaves as an electrolyte producing three chloride ions outside the coordination sphere. The oxidation state of cobalt in the complex is:

ISC 2018

(a) +2

(b) +3

(c) 0

(d) +1

Ans : (b) +3

Ammonia is a neutral ligand and contributes no charge. Since three chloride ions exist outside the coordination sphere, the complex ion must possess charge +3. Therefore oxidation state of cobalt in $[Co(NH_3)_6]^{3+}$ is calculated as +3according to coordination compound charge balance principles.

10. In the complex $[Ni(CN)_4]^{2-}$, cyanide ion causes pairing of electrons because it is:

ISC 2001

(a) A weak field ligand

(b) A neutral ligand

(c) A strong field ligand

(d) An ambidentate ligand only

Ans : (c) A strong field ligand

Cyanide ion belongs to the strong field region of the spectrochemical series. Strong field ligands

NODIA

(a) Both A and R are true and R is the correct explanation of A

(b) Both A and R are true but R is not the correct explanation of A

(c) A is true but R is false

(d) A is false but R is true

Ans : (b) Both A and R are true but R is not the correct explanation of A

EDTA contains six donor atoms capable of coordinate bond formation with a single metal ion. Formation of multiple coordinate bonds produces stable chelate rings and greatly enhances stability of the coordination compound due to chelate effect.

33. Assertion (A) : In anionic complexes, the metal name generally ends with "–ate".

Reason (R) : The coordination entity possesses negative charge.

ISC 2024

(a) Both A and R are true and R is the correct explanation of A

(b) Both A and R are true but R is not the correct explanation of A

(c) A is true but R is false

(d) A is false but R is true

Ans : (c) A is true but R is false

According to IUPAC nomenclature rules, negatively charged coordination entities require modification of the metal name ending into "–ate". Examples include ferrate, cuprate and argentate. This rule applies specifically to anionic complexes present in coordination compounds.

34. Assertion (A) : The complex $[Pt(NH_3)_2Cl_2]$ exhibits geometrical isomerism.

Reason (R) : Ligands can occupy different relative positions around platinum.

ISC 2018

(a) Both A and R are true and R is the correct explanation of A

(b) Both A and R are true but R is not the correct explanation of A

(c) A is true but R is false

(d) A is false but R is true

Ans : (d) A is false but R is true

In square planar complexes, ligands may occupy adjacent cis positions or opposite trans positions relative to each other. Such variation in spatial arrangement around the platinum atom produces geometrical isomerism, giving rise to compounds with different physical and biological properties.

35. Assertion (A) : Werner's secondary valencies are directional in nature.

Reason (R) : Secondary valencies determine the geometry of coordination compounds.

ISC 2025

(a) Both A and R are true and R is the correct explanation of A

(b) Both A and R are true but R is not the correct explanation of A

(c) A is true but R is false

(d) A is false but R is true

Ans : (a) Both A and R are true and R is the correct explanation of A

Secondary valencies correspond to the coordination number of the central metal ion and are satisfied by ligands. These valencies possess directional character and therefore determine definite spatial arrangement and geometry of ligands in coordination compounds according to Werner's coordination theory.

36. Assertion (A) : Crystal field theory explains the colour of coordination compounds.

Reason (R) : Splitting of d-orbitals permits d–d electronic transitions.

ISC 2013

(a) Both A and R are true and R is the correct explanation of A

(b) Both A and R are true but R is not the correct explanation of A

(c) A is true but R is false

(d) A is false but R is true

Ans : (b) Both A and R are true but R is not the correct explanation of A

Ligands surrounding the central metal ion split the degenerate d-orbitals into different energy levels. Electrons absorb visible light and undergo d–d transitions between these split orbitals. Such transitions are responsible for the characteristic colours shown by many coordination compounds.

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(c) Behaves as weak field ligand only

(d) Produces tetrahedral complexes only

Ans : (a) Possesses six donor atoms capable of coordinate bonding

EDTA is a hexadentate ligand containing six donor atoms capable of simultaneously coordinating with the central metal ion. Formation of multiple coordinate bonds produces highly stable ring structures known as chelates, greatly increasing stability of the coordination compound through chelate effect.

17. In the complex $[Cr(H_2O)_6]Cl_3$, water molecules behave as:

ISC 2010

(a) Counter ions

(b) Monodentate ligands

(c) Bidentate ligands

(d) Ambidentate ligands

Ans : (b) Monodentate ligands

Water molecules contain one oxygen atom possessing a lone pair available for donation to the central metal ion through one donor atom. Therefore each H_2O molecule forms only one coordinate bond with chromium and behaves as a monodentate ligand in the coordination complex.

18. In the spectrochemical series, ligands producing maximum crystal field splitting are generally:

ISC 2011

(a) Weak field ligands

(b) Strong field ligands

(c) Monodentate ligands only

(d) Negatively charged ligands only

Ans : (b) Strong field ligands

Strong field ligands produce large crystal field splitting energy by causing greater separation between lower and higher d-orbitals. Such ligands frequently induce pairing of electrons in lower orbitals and form low-spin complexes according to crystal field theory.

19. In crystal field theory, splitting of d-orbitals occurs because:

ISC 2006

(a) Ligands chemically combine with d-electrons permanently

(b) Electrostatic interactions remove degeneracy of d-orbitals

(c) Metal ions lose all valence electrons

(d) d-Orbitals become completely filled in complexes

Ans : (b) Electrostatic interactions remove degeneracy of d-orbitals

According to crystal field theory, ligands approaching the central metal ion produce electrostatic repulsions with d-electrons. Since some d-orbitals experience greater repulsion than others depending on orientation, degeneracy is removed and d-orbitals split into different energy levels called crystal field splitting.

20. A student observed that the complex $[Ni(CO)_4]$ is diamagnetic although nickel generally forms paramagnetic compounds. This is because in the complex:

ISC 2024

(a) Carbon monoxide acts as a strong field ligand causing electron pairing

(b) Nickel loses all d-electrons completely

(c) Carbon monoxide behaves as bidentate ligand

(d) Nickel attains oxidation state $+4$

Ans : (a) Carbon monoxide acts as a strong field ligand causing electron pairing

Carbon monoxide is a strong field ligand and produces large crystal field splitting energy. This causes pairing of electrons in the d-orbitals of nickel. As a result all electrons become paired in $[Ni(CO)_4]$, making the complex diamagnetic despite nickel usually forming paramagnetic compounds.

21. The complex $[Pt(NH_3)_2Cl_2]$ shows cis and trans forms because:

ISC 2017

(a) Ligands occupy different relative positions around platinum

(b) Chloride ions are present outside coordination sphere

(c) Ammonia behaves as ambidentate ligand

(d) Platinum changes oxidation state continuously

Ans : (a) Ligands occupy different relative positions around platinum

Geometrical isomerism arises when ligands occupy different spatial positions around the central metal ion. In square planar complexes like $[Pt(NH_3)_2Cl_2]$, identical ligands may occupy adjacent cis positions or opposite trans positions,

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resulting in distinct geometrical isomers having different physical and chemical properties.

22. The complex $[Co(en)_3]^{3+}$ exhibits optical isomerism because:

ISC 2002

(a) It forms non-superimposable mirror images

(b) Ethylenediamine behaves as monodentate ligand

(c) Cobalt exists in zero oxidation state

(d) The complex possesses square planar geometry

Ans : (a) It forms non-superimposable mirror images

The octahedral complex $[Co(en)_3]^{3+}$ contains three bidentate ethylenediamine ligands arranged asymmetrically around the cobalt ion. Consequently the complex exists as two non-superimposable mirror images called enantiomers, which exhibit optical isomerism and rotate plane polarised light in opposite directions.

23. The complex $K_4[Fe(CN)_6]$ is more stable than $[Fe(H_2O)_6]^{2+}$ mainly because:

ISC 2021

(a) Cyanide ion produces stronger metal–ligand bonding

(b) Water behaves as bidentate ligand

(c) Iron loses all electrons completely

(d) Coordination number decreases significantly

Ans : (a) Cyanide ion produces stronger metal–ligand bonding

Cyanide ion is a strong field ligand and forms strong coordinate bonds with the central metal ion through effective overlap and back bonding. Consequently complexes containing cyanide ligands possess much greater thermodynamic stability compared to complexes formed with weak ligands such as water molecules.

24. The ligand SCN^- can coordinate through sulphur or nitrogen atom. Such ligands are called:

ISC 2025

(a) Chelating ligands

(b) Neutral ligands

(c) Ambidentate ligands

(d) Hexadentate ligands

Ans : (c) Ambidentate ligands

Ambidentate ligands possess two different donor atoms capable of coordinate bond formation with the central metal ion. Thiocyanate ion can coordinate either through sulphur atom or nitrogen atom, resulting in formation of linkage isomers in coordination compounds.

NODIA

25. According to crystal field theory, tetrahedral complexes generally show smaller crystal field splitting than octahedral complexes because:

ISC 2010

(a) Ligands approach between the axes in tetrahedral geometry

(b) Tetrahedral complexes contain no d-electrons

(c) All tetrahedral complexes are diamagnetic

(d) Octahedral complexes possess lower coordination number

Ans : (a) Ligands approach between the axes in tetrahedral geometry

In tetrahedral complexes, ligands approach between the coordinate axes where electron density of d-orbitals is lower. Consequently electrostatic repulsion between ligands and d-electrons becomes smaller, producing lower crystal field splitting energy compared to octahedral complexes.

26. The complex $[Cu(NH_3)_4]^{2+}$ appears deep blue because:

ISC 2024

(a) Ammonia completely removes d-electrons from copper

(b) d–d electronic transitions absorb visible light

(c) Copper attains noble gas configuration

(d) The complex becomes tetrahedral only

Ans : (b) d–d electronic transitions absorb visible light

In coordination complexes, ligands split the degenerate d-orbitals into different energy levels. Electrons absorb specific wavelengths of visible light and undergo d–d transitions between these split orbitals, producing characteristic colours such as the deep blue colour of $[Cu(NH_3)_4]^{2+}$.

27. Assertion (A) : Coordination compounds retain their identity in aqueous solution.

Reason (R) : Ligands remain bonded to the central metal ion through coordinate bonds.

ISC 2020

(a) Both A and R are true and R is the correct explanation of A

(b) Both A and R are true but R is not the correct explanation of A

(c) A is true but R is false

(d) A is false but R is true

Ans : (a) Both A and R are true and R is the correct explanation of A

Coordination compounds do not dissociate completely in aqueous solution because ligands remain attached to the central metal ion through coordinate covalent bonds. Hence the coordination entity retains its identity in solution unlike double salts which dissociate completely into constituent ions.

28. Assertion (A) : The complex $[Fe(CN)_6]^{4-}$ is diamagnetic.

Reason (R) : Cyanide ion is a strong field ligand causing pairing of electrons.

ISC 2023

(a) Both A and R are true and R is the correct explanation of A

(b) Both A and R are true but R is not the correct explanation of A

(c) A is true but R is false

(d) A is false but R is true

Ans : (b) Both A and R are true but R is not the correct explanation of A

Cyanide ion belongs to the strong field region of the spectrochemical series and produces large crystal field splitting energy. This forces d-electrons to pair in lower orbitals, leaving no unpaired electrons and making the complex diamagnetic in nature.

29. Assertion (A) : The complex $[Co(en)_3]^{3+}$ exhibits optical isomerism.

Reason (R) : The complex forms non-superimposable mirror images.

ISC 2014

(a) Both A and R are true and R is the correct explanation of A

(b) Both A and R are true but R is not the correct explanation of A

(c) A is true but R is false

(d) A is false but R is true

Ans : (c) A is true but R is false

Optical isomerism arises due to formation of non-superimposable mirror images called enantiomers. In $[Co(en)_3]^{3+}$, three bidentate ligands produce asymmetric arrangement around the central metal ion, resulting in optical activity and rotation of plane polarised light.

30. Assertion (A) : Strong field ligands generally form low-spin complexes.

Reason (R) : Strong field ligands produce large crystal field splitting energy.

ISC 2010

(a) Both A and R are true and R is the correct explanation of A

(b) Both A and R are true but R is not the correct explanation of A

(c) A is true but R is false

(d) A is false but R is true

Ans : (d) A is false but R is true

Strong field ligands cause large splitting of d-orbitals. Due to this large crystal field splitting energy, electrons pair in lower energy orbitals instead of occupying higher orbitals singly. Consequently low-spin inner orbital complexes are generally formed in presence of strong field ligands.

31. Assertion (A) : The complex $[NiCl_4]^{2-}$ is paramagnetic.

Reason (R) : Chloride ion acts as a weak field ligand.

ISC 2018

(a) Both A and R are true and R is the correct explanation of A

(b) Both A and R are true but R is not the correct explanation of A

(c) A is true but R is false

(d) A is false but R is true

Ans : (a) Both A and R are true and R is the correct explanation of A

Chloride ion is a weak field ligand and produces small crystal field splitting energy. Therefore electrons remain unpaired instead of pairing in lower orbitals. Presence of unpaired electrons makes the complex $[NiCl_4]^{2-}$ paramagnetic according to crystal field theory.

32. Assertion (A) : EDTA forms highly stable complexes with metal ions.

Reason (R) : EDTA behaves as a hexadentate ligand.

ISC 2011

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15. A hydrated iron complex behaves as a high-spin complex. Which property of water ligand causes this behaviour?

ISC 2003

Ans :

Water is a weak field ligand.

16. A square planar platinum complex exhibited cis and trans forms. Why is geometrical isomerism possible in such complexes?

ISC 2020

Ans :

Ligands can occupy different relative positions around the metal ion.

17. Chelating ligands generally produce more stable complexes than monodentate ligands. What is the main reason for this increased stability?

ISC 2014

Ans :

Formation of stable ring structures around the metal ion.

18. A nitrite ligand formed two different complexes by bonding through nitrogen and oxygen atoms separately. Which special property of the ligand is responsible?

ISC 2001

Ans :

Ambidentate character.

19. According to Werner's theory, ligands attached directly to the metal ion do not ionise in solution. Which valencies do these ligands satisfy?

ISC 2003

Ans :

Secondary valencies.

20. The colour of many coordination compounds changes when ligands are replaced. Which factor mainly causes this variation?

ISC 2016

Ans :

Change in crystal field splitting energy.

21. Addition of ammonia to copper sulphate solution produces a deep blue complex. Which electronic phenomenon is mainly responsible for this colour?

ISC 2009

Ans :

d–d electronic transitions.

22. A cobalt complex containing strong field ligands showed low magnetic moment. What effect do strong field ligands produce on d-electrons?

ISC 2024

Ans :

Electron pairing in lower energy orbitals.

23. In the complex $[Co(en)_2Cl_2]^+$, why is the coordination number equal to six?

ISC 2021

Ans :

Because the ligands occupy six donor positions around cobalt.

24. During ionisation of coordination compounds, certain ions separate easily in solution. Which ions undergo ionisation first?

ISC 2023

Ans :

Counter ions outside the coordination sphere.

25. An iron complex containing cyanide ligands showed lower magnetic moment than a fluoride complex. What property of cyanide ion causes this effect?

ISC 2000

Ans :

Strong field nature causing electron pairing.

NODIA

26. Metal carbonyl complexes are generally diamagnetic. Which property of carbon monoxide ligand is responsible?

ISC 2005

Ans :

Strong field character of carbon monoxide.

27. A tetrahedral complex showed weaker crystal field splitting compared to an octahedral complex. What is the reason for this difference?

ISC 2015

Ans :

Ligands approach between the coordinate axes in tetrahedral geometry.

28. In medicinal chemistry, only cis-platin acts as an anticancer drug. What structural feature makes cis-platin biologically active?

ISC 2010

Ans :

Cis arrangement of ligands around platinum.

FILL IN THE BLANK

1. The coordination number and oxidation state of the complex $K_4[Fe(CN)_6]$ are _____ and _____ respectively.
ISC 2023

Ans :
6, 2

2. In coordination complexes, the central metal atom or ion behaves as _____ and the ligands behave as _____.
ISC Specimen 2023

Ans :
Lewis acid, Lewis base

3. Coordination compounds structure was first proposed by _____.
ISC 2009

Ans :
Coordination compounds structure was first proposed by Alfred Werner.

4. Paramagnetic compounds are generally _____ and contain _____ electrons.
ISC 2021-22 (Sem-II)

Ans :
coloured, unpaired

5. Outer orbital complexes involve _____ hybridisation and are _____ spin complexes.
ISC 2020

Ans :
sp^3d^2, high.

ONE MARK QUESTIONS

6. Write the IUPAC name of $[Co(NH_3)_4Cl_2]Cl$
ISC 2021-22 (Sem-II)

Ans :
Tetraaminedichlorocobalt (IV) chloride.

7. A chemist found that $[Fe(CN)_6]^{4-}$ is diamagnetic. Which property of cyanide ion is responsible for this observation?
ISC 2014

Ans :
Cyanide ion is a strong field ligand causing electron pairing.

8. In chemotherapy, cis-platin is therapeutically active whereas trans-platin is ineffective. Which type of isomerism explains this difference?
ISC 2018

Ans :
Geometrical isomerism.

9. While studying optical activity, a student observed that $[Co(en)_3]^{3+}$ rotates plane polarised light. What structural feature causes this behaviour?
ISC 2024

Ans :
Presence of non-superimposable mirror images.

10. During estimation of water hardness, EDTA is commonly used. Which property of EDTA makes it suitable for this purpose?
ISC 2011

Ans :
Ability to form highly stable chelate complexes.

11. A coordination compound of nickel containing chloride ligands was found to be tetrahedral and paramagnetic. What is the nature of chloride ligand responsible for this behaviour?
ISC 2018

Ans :
Weak field ligand.

12. Two nickel complexes, $[Ni(CN)_4]^{2-}$ and $[NiCl_4]^{2-}$, show different magnetic behaviour. What causes this difference?
ISC 2022

Ans :
Difference in crystal field strength of ligands.

13. In coordination chemistry, ligands are often described as Lewis bases. What characteristic of ligands supports this description?
ISC 2010

Ans :
Donation of lone pair electrons.

14. A metal ion surrounded by ligands showed splitting of d-orbitals into two energy levels. Which theory explains this phenomenon?
ISC 2025

Ans :
Crystal field theory.

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9.1 Biological System

1. Chlorogphyll is a coordination compound of Mg.
2. Haemoglobin of blood is a coordination compound of Fe.
3. Vitamin of B_{12} is a coordination compound of Co.

9.2 Analytical Chemistry

1. Presence of Co^{2+} ion is tested by $K_3[Fe(CN)_6]$
2. Presence of Fe^{3+} ion is tested by $K_4[Fe(CN)_6]$
3. In volumetric analysis EDTA is used.
4. The hardness of water is estimated by complexometric titration.

9.3 Medicinal Chemistry

1. EDTA is used for treatment of lead poisoning.
2. The platinum complex cis-platin $[Pt(NH_3)_2Cl_2]$ is used in cancer therapy.

9.4 Extraction of Metals

Metals like silver and gold are extracted from their ores through the formation of cyanide complexes $[Ag(CN)_2]^-$ and $[Au(CN)_2]^-$ respectively.

The ore is treated with a dilute solution of NaCN or KCN in the presence of air, forming these stable complexes, from which the metal is later recovered by displacement with zinc.

****

OBJECTIVE QUESTIONS

1. The hybridisation of the iron atom in $[Fe(CN)_6]^{3-}$ complex is

ISC 2010

(a) sp^3 (b) d^2sp^3

(c) sp^3d^2 (d) dsp^2

Ans : (b) d^2sp^3

Coordination number of complex is 6 and CN^- is a strong field ligand which paired up the *d*-electrons of the metal. So, hybridisation is d^2sp^3.

2. Among the following coordination compounds, the one giving a white precipitate with $BaCl_2$ solution is

ISC 2012

(a) $[Cr(H_2O)_5Br]SO_4$ (b) $[Cr(H_2O)_5SCN]$

(c) $[Co(NH_3)_5SO_4]Br$ (d) $[Pt(NH_3)_6Cl_4]$

Ans : (a) $[Cr(H_2O)_5Br]SO_4$

$[Cr(H_2O)_5Br]SO_4$ gives a white precipitate of $BaSO_4$ when reacted with $BaCl_2$ solution, as it gives SO_4^{2-} ions in solution.

3. The type of hybridisation involved in octahedral complexes is

ISC Specimen 2021-22 (Sem-II)

(a) sp^3 (b) dsp^2

(c) sp^3d (d) d^2sp^3

Ans : (d) d^2sp^3

An octahedral complex has a coordination number of 6, requiring 6 hybrid orbitals.

The hybridisation involved is d^2sp^3 (using 2 inner d-orbitals), giving an octahedral geometry with bond angles of 90°.

Other options: sp^3 → tetrahedral, dsp^2 → square planar, sp^3d → trigonal bipyramidal.

4. The coordination number of cobalt in $[Co(en)_2Cl_2]^+$ is:

ISC 2018

(a) 2 (b) 4

(c) 6 (d) 8

Ans : (c) 6

Ethylenediamine is a bidentate ligand and each molecule forms two coordinate bonds with the central metal ion. Two ethylenediamine ligands contribute four coordination positions while two chloride ligands contribute two more, giving total coordination number 6.

NODIA

29. A chromium aqua complex appeared coloured in aqueous solution. Which electronic configuration feature is responsible for this observation?

ISC 2025

Ans :

Presence of partially filled d-orbitals.

30. Ethylenediamine behaves as a neutral bidentate ligand. Which structural feature allows this behaviour?

ISC 2020

Ans :

Presence of two donor nitrogen atoms.

31. Coordination compounds are important in extraction of metals from ores. Which property of complexes is utilised in metallurgy?

ISC 2011

Ans :

Selective complex formation with metal ions.

32. A cobalt complex containing six ammonia molecules showed octahedral geometry. Which factor determines this geometry?

ISC 2024

Ans :

Coordination number six around cobalt.

33. Linkage isomerism is commonly shown by ligands like SCN^-. What property of such ligands enables this behaviour?

ISC 2000

Ans :

Ability to coordinate through different donor atoms.

34. An iron complex containing water ligands showed paramagnetic behaviour. What feature of the metal ion causes this property?

ISC 2016

Ans :

Presence of unpaired electrons.

35. In qualitative inorganic analysis, coordination compounds are widely used for identification of metal ions. Which property makes them useful for this purpose?

ISC 2023

Ans :

Formation of characteristic coloured complexes.

36. During conductivity testing, a student observed that $[Co(NH_3)_6]Cl_3$ produces three chloride ions in solution. What does this indicate about the position of chloride ions in the compound?

ISC 2023

Ans :

The chloride ions are present outside the coordination sphere.

37. Name the types of isomerism shown by the following pairs of compounds:

ISC 2017

(i) $[Cu(NH_3)_4][PtCl_4]$ and $[Pt(NH_3)_4][CuCl_4]$

(ii) $[Co(Pn)_2Cl_2]^+$ and $[Co(Tn)_2Cl_2]^+$

Ans :

(i) Coordination isomerism

(ii) Ligand isomerism

38. Correct the following statement by changing the underlined part of sentence.

In a coordination complex, donation of electron pair takes place from the central metal atom to the ligands.

ISC 2009

Ans :

In a coordination complex, donation of electron pair takes place from the ligands to the central metal atom.

TWO MARKS QUESTIONS

39. Give the IUPAC name for the following.

ISC 2011

(i) $Na_3[AlF_6]$ (ii) $[CO(NH_3)_6]Cl_3$

Ans :

(i) Sodiumhexafluoroaluminate (III)

(ii) Hexaamminecobalt (III) chloride

40. Write the IUPAC names of the following.

(a) $[Co(NH_3)_4SO_4]NO_3$

(b) $K[Pt(NH_3)Cl_3]$

ISC 2017

Ans :

(a) Tetraaminesulphatecobalt (III) nitrate

(b) Potassiumaminetrichloroplatinate (II)

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$[Co(NH_3)_5SO_4]Br + AgNO_3(aq) \longrightarrow$

$[Co(NH_3)_5SO_4]NO_3 + \underset{\text{Yellow ppt.}}{AgBr(s)\downarrow}$

$[Co(NH_3)_5Cl]SO_4 + AgNO_3(aq) \longrightarrow$ No reaction

These two tests prove that the given two compounds are a pair of ionisation isomers.

76. For the complex ion of $[Fe(CN)_6]^{3-}$

(i) Show hybridisation diagramatically.

(ii) Is it an inner orbital complex or an outer orbital complex?

(iii) State its magnetic property.

ISC 2011

Ans :

(i) Let the oxidation number of Fe in the complex ion $[Fe(CN)_6]^{3-}$ be x.

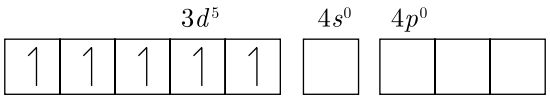
Then, $x + 6(-1) = -3$

$x = +3$

Electronic configuration

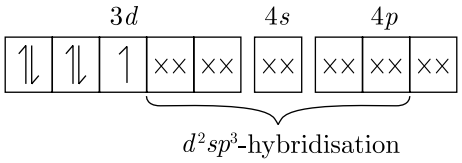
$Fe = [Ar]3d^6 4s^2$

For Fe^{3+}



CN^- being strong field ligand, paired up the d-electrons of the metal

For $[Fe(CN)_6]^{3-}$ =



Six pairs of electrons from six CN^- ions.

(ii) It is an inner orbital complex as inner d-orbitals take part in hybridisation.

(iii) It is paramagnetic due to the presence of unpaired electron.

FOUR MARKS QUESTIONS

77. A coordination compound gave one mole of AgCl precipitate per mole of the compound on treatment with excess $AgNO_3$ solution. The compound has the formula $[Co(NH_3)_5Cl]Cl_2$. Explain the observation and determine the number of ionisable chloride ions present.

ISC 2020

Ans :

In $[Co(NH_3)_5Cl]Cl_2$, one chloride ion is present inside the coordination sphere while two chloride ions are present outside the coordination sphere.

Only chloride ions outside the coordination sphere ionise in aqueous solution and react with $AgNO_3$ to form AgCl precipitate.

Therefore the compound contains two ionisable chloride ions.

78. The complexes $[Fe(CN)_6]^{4-}$ and $[FeF_6]^{4-}$ show different magnetic behaviour although iron exists in the same oxidation state in both complexes. Explain the reason using crystal field theory.

ISC 2023

Ans :

In $[Fe(CN)_6]^{4-}$, cyanide ion acts as a strong field ligand and produces large crystal field splitting energy. Electrons pair in lower energy orbitals, making the complex low-spin and diamagnetic.

In $[FeF_6]^{4-}$, fluoride ion is a weak field ligand producing small splitting energy. Electrons remain unpaired, resulting in paramagnetic behaviour.

79. Explain why $[Ni(CN)_4]^{2-}$ possesses square planar geometry whereas $[NiCl_4]^{2-}$ possesses tetrahedral geometry.

ISC 2019

Ans :

In $[Ni(CN)_4]^{2-}$, cyanide ion is a strong field ligand and causes pairing of d-electrons. This favours dsp^2 hybridisation and square planar geometry.

In $[NiCl_4]^{2-}$, chloride ion is a weak field ligand and does not cause pairing. Therefore sp^3 hybridisation occurs, producing tetrahedral geometry.

80. Explain the importance of chelation in coordination compounds with reference to EDTA.

ISC 2024

Ans :

Chelation occurs when a polydentate ligand forms ring structures with a central metal ion.

EDTA is a hexadentate ligand capable of forming highly stable chelate complexes with metal ions.

Because of high stability, EDTA is extensively used in estimation of water hardness and in complexometric titrations involving calcium and magnesium ions.

NODIA

51. For the complex ion $[Co(NH_3)_6]^{3+}$, state the oxidation state of central metal atom and the coordination number of the complex ion.

ISC Specimen 2021-22 (Sem-1w)

Ans :

Let, the oxidation state of Co in the complex $[Co(NH_3)_6]^{3+}$ be x.

$$x + 6 \times 0 = +3$$

$$x = +3$$

As six ammonia molecule is attached to Co (central metal). Thus, coordination number is 6.

52. $[Fe(CN)_6]^{4-}$ is a coordination complex ion.

(a) Calculate the oxidation number of iron in the complex.

(b) Write the IUPAC name of the complex ion.

ISC 2019

Ans :

$[Fe(CN)_6]^{4-}$ ion

(a) Let the oxidation number of iron in the complex, $[Fe(CN)_6]^{4-}$ be x.

$$x + 6(-1) = -4, \Rightarrow x - 6 = -4$$

$$x = 6 - 4 = 2$$

(b) Hexacyanoferrate(II)

53. When a coordination compound $COCl_3.6NH_3$ is mixed with $AgNO_3$, three moles of AgCl are precipitated per mole of the compound. Write the structural formula and IUPAC name of the coordination compound.

ISC 2019

Ans :

On mixing the coordination compound, $COCl_3 \cdot 6NH_3$ with $AgNO_3$, three moles of AgCl are precipitated. It indicates the presence of three chlorine atoms outside the coordination sphere, i.e. 3 moles of chlorine are ionisable. Therefore, structural formula of the given complex is $[CO(NH_3)_6]Cl_3$. IUPAC name of the complex is hexaamminecobalt (III) chloride.

54. State the hybridisation and magnetic property Write the IUPAC names of the following coordination compounds.

(i) $[Cr(NH_3)_4(H_2O)_2]Cl_3$

(ii) $[PtCl_2(NH_3)_4][PtCl_4]$

ISC 2015

Ans :

IUPAC name

(i) $[Cr(NH_3)_4(H_2O)]Cl_3$

Teraamminediaquachromium (III) chloride

(ii) $[PtCl_2(NH_3)_4][PtCl_4]$

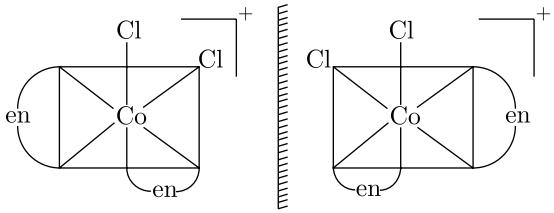
Tetraamminedichloroplatinum (IV) tetrachloroplatinate (II)

55. Write the structures of optical isomers of the complex ion $[Co(en)_2Cl_2]^+$.

ISC 2021-22 (Sem-II), 2015, 2013

Ans :

Cis-form of $[Co(en)_2Cl_2]^+$ give optical isomers.



Non-superimposable mirror image structure

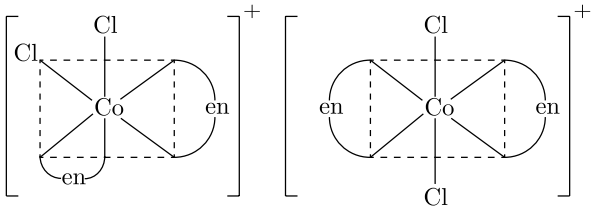
56. Write the IUPAC name of $[Co(en)_2Cl_2]^+$ ion and draw the structures of its geometrical isomers.

ISC 2018

Ans :

IUPAC name : Dichloro bis-(ethane-1, 2-diamine) cobalt(III) ion.

Structure of its geometrical isomers (cis and trans) are given below.



cis *trans*

57. Name the type of isomerism shown by each of the following pairs of compounds.

ISC Specimen 2021-22 (Sem-II)

(i) $[CoCl_2(NH_3)_4]Cl.H_2O$ and $[CoCl(H_2O)(NH_3)_4]Cl_2$

(ii) $[Cr(NH_3)_5Br]SO_4$ and $[Cr(NH_3)_5SO_4]Br$

Ans :

(i) Given compounds show hydrate isomerism. These type of isomerism are shown by those isomers which have same composition but different number of water molecules attached to metal ion.

NODIA

88. Explain why secondary valencies are considered directional according to Werner's coordination theory.

ISC 2003

Ans :

Secondary valencies correspond to coordination number and are satisfied by ligands directly attached to the metal ion.

These valencies possess fixed orientation in space around the central atom.

Hence they determine the geometry and spatial arrangement of ligands in coordination compounds.

89. Explain the role of coordination compounds in metallurgy with suitable examples.

ISC 2025

Ans :

Coordination compounds are extensively used in extraction and purification of metals.

Gold and silver are extracted through cyanide process involving formation of soluble cyanide complexes.

Nickel is purified in Mond's process through formation of volatile nickel tetracarbonyl complex $Ni(CO)_4$.

These methods utilise selective complex formation and decomposition reactions.

90. Explain the hybridisation, geometry and magnetic behaviour of $[Fe(CN)_6]^{4-}$ using valence bond theory.

ISC 2000

Ans :

In $[Fe(CN)_6]^{4-}$, iron exists in $+2$ oxidation state.

Cyanide ion is a strong field ligand and causes pairing of d-electrons.

The complex undergoes d^2sp^3 hybridisation involving inner d-orbitals.

Hence octahedral geometry is formed.

Since all electrons become paired, the complex behaves as diamagnetic.

91. Explain crystal field splitting in octahedral complexes. How does crystal field splitting influence magnetic behaviour of coordination compounds?

ISC 2011

Ans :

In octahedral complexes, ligands approach the metal ion along coordinate axes.

As a result, d-orbitals split into two sets of different energies:

$t_{2g}(d_{xy}, d_{yz}, d_{xz})$ and $e_g(d_{x^2-y^2}, d_{z^2})$.

The energy difference between these sets is called crystal field splitting energy (Δ_o).

If Δ_o is large, electrons pair in lower orbitals producing low-spin diamagnetic complexes.

If Δ_o is small, electrons remain unpaired producing high-spin paramagnetic complexes.

92. Explain the biological and medicinal importance of coordination compounds with suitable examples.

ISC 2020

Ans :

Coordination compounds play important roles in biological systems.

Haemoglobin is an iron coordination compound responsible for oxygen transport.

Chlorophyll is a magnesium complex essential for photosynthesis.

Vitamin B_{12} contains cobalt coordination compound necessary for metabolism.

Cis-platin, a platinum coordination compound, is widely used as an anticancer drug in chemotherapy.

93. Differentiate between double salts and coordination compounds on the basis of ionisation behaviour, identity in solution and examples.

ISC 2004

Ans :

Double Salts	**Coordination Compounds**
Dissociate completely in solution	Retain identity in solution
Constituent ions exist independently	Coordination entity remains intact
Lose characteristic properties in solution	Maintain characteristic properties
Example: Mohr's salt	Example: $[Co(NH3)6]Cl3$

94. Explain the formation of geometrical isomerism in octahedral complexes with suitable example.

ISC 2009

Ans :

Geometrical isomerism arises because ligands occupy different positions around the central metal ion.

In octahedral complexes, identical ligands may occupy adjacent cis positions or opposite trans positions.

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(b) In both compounds, ambidentate ligand SCN is present.

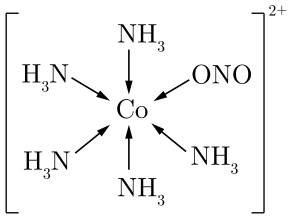
In $[Cr(SCN)(H_2O)_5]^{2+}$ complex SCN is attached through S with Cr while in $[Cr(NCS)(H_2O)_5]^{+2}$ complex SCN is attached through -N- . Hence, they show linkage isomerism.

64. Draw the structural isomer of $[Co(NH_3)_5NO_2]Cl_2$ and name the type of isomerism.

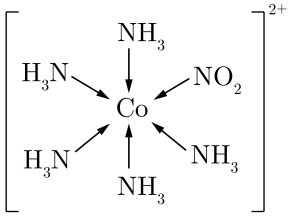
ISC 2012

Ans :

The isomerism is linkage isomerism, i.e. more than one atom in a monodentate ligand may functions as donor. For this, in NO_2^- ion, either nitrogen or an oxygen atom may functions as donor.



Pentaamminemtrito-O-cobalt (III) ion



Pentaamminenitro-N-cobalt (III) ion

65. What type of isomers are $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5SO_4]Br$? Give a chemical test to distinguish between them.

ISC 2021-22 (Sem-II), 2015, 2013

Ans :

The compounds will give different ions in solution, although they have same composition. Hence, they represent ionisation isomers. These compounds ionise in solution as given below

$$[CoBr(NH_3)_5]SO_4 \longrightarrow [CoBr(NH_3)_5]^{2+} + SO_4^{2-}$$

$$[Co(SO_4)(NH_3)_5]Br \longrightarrow [Co(SO_4)(NH_3)_5]^{+} + Br^{-}$$

The complex $[CoBr(NH_3)_5]SO_4$ is red violet and its aqueous solution gives a white precipitate of $BaSO_4$ with $BaCl_2$. Thus this reaction confirms the presence of SO_4^{2-} ions in the solution. Whereas the complex $[Co(SO_4)(NH_3)_5]Br$ is red in colour and its aqueous solution gives a light yellow precipitate of AgBr with $AgNO_3$ thus confirming the presence of Br^- ions in the solution.

$$\underset{\text{Red violet}}{[CoBr(NH_3)_5]SO_4} + BaCl_2 \longrightarrow \text{White ppt. due to } SO_4^{2-} \text{ ion}$$

$$\underset{\text{Red}}{[Co(NH_3)_5SO_4]Br} + BaCl_2 \longrightarrow \text{No ppt.}$$

66. $[Fe(CN)_6]^{4-}$ is a coordination complex ion.

ISC 2021-22 (Sem-II), 2019

(i) Is the complex ion diamagnetic or paramagnetic ?

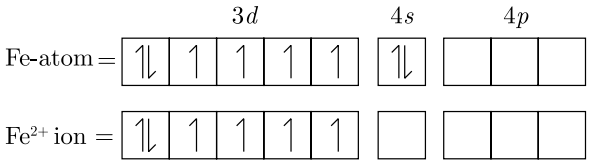
(ii) What is the hybridisation state of the central metal atom?

Ans :

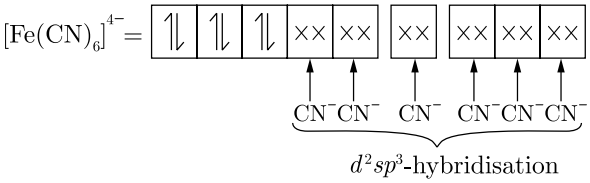
(i) In the complex $[Fe(CN)_6]^{4-}$, iron exists in the + 2 oxidation state. Electronic configuration of Fe^{2+} is $4s^0 3d^6$. As CN^- is a strong field ligand, it causes the pairing of the unpaired $3d$ electrons.

Hence, it is diamagnetic.

(ii) In the given complex, hybridisation state of the central metal atom is d^2sp^3.



CN^- is a strong field ligand, thus it can pair the unpaired electrons of Fe^{2+}.



67. $[CoF_6]^{3-}$ is a coordination complex ion.

(i) What is the oxidation number of cobalt in the complex?

(ii) How many unpaired electrons are there in the complex?

(iii) State the magnetic behaviour of the complex.

(iv) Give the IUPAC name of the complex.

ISC 2012

NODIA

41. Write the IUPAC names of the following complexes.

ISC 2010

(a) $[Co(NH_3)_4(H_2O)_2]Cl_3$ (b) $K_2[Ni(CN)_4]$

Ans :

(a) Tetraaminediaquacobalt (III) chloride.

(b) Potassium tetracyanonickelate (II).

42. Write the formula of the following compounds.

(i) Triamminetriaquachromium (III) chloride

(ii) Potassiumhexacyanoferrate (III)

ISC 2014

Ans :

(i) $[Cr(NH_3)_3(H_2O)_3]Cl_3$

(ii) $K_3[Fe(CN)_6]$

43. Write the formula of the following compounds.

(i) Potassiumtrioxalatoaluminate (III)

(ii) Hexaaquairon (II) sulphate

ISC 2017

Ans :

(i) $K_3[Al(ox)_3]$ or $K_3[Al(C_2O_4)_3]$

(ii) $[Fe(H_2O)_6]SO_4$

44. Write the formula of the following coordination compound.

(i) Tetracarbonylnickel (0)

(ii) Potassiumdicyanoargentate (I)

1SC 2010

Ans :

(i) $[Ni(CO_4)]$ (ii) $K[Ag(CN)_2]$

45. Write the IUPAC names of the following.

(a) $K_3[Fe(C_2O_4)_3]$

(b) $[Co(NH_3)_5Cl]SO_4$

ISC 2019

Ans :

(a) $K_3[Fe(C_2O_4)_3]$

Potassiumtrioxalato ferrate (III)

(b) $[Co(NH_3)_5Cl]SO_4$

Pentaamminechlorocobalt(III) sulphate

46. Give the IUPAC names of the following coordination compounds.

ISC 2013

(i) $K_2[Zn(OH)_4]$

(ii) $[Co(NH_3)_5(CO_3)]Cl_3$

Ans :

(i) Potassiumtetrahydroxyzincate (II)

(ii) Pentaamminecarbonatocobalt (III) chloride

47. Write the formula of the following coordination compounds.

(i) Potassiumtetracyanonickelate (0)

(ii) Triamminetrinitrocobalt (III)

ISC 2012

Ans :

(i) $K_4[Ni(CN)_4]$

(ii) $[CO(NH_3)_3(NO_2)_3]$

48. Write the formula of each of the following compounds.

(a) Potassium trioxalatoaluminate (III)

(b) Triammine triaquachromium (III) chloride

ISC Specimen 2021-22 (Sem-1w)

Ans :

(a) $K_3[Al(C_2O_4)_3]$

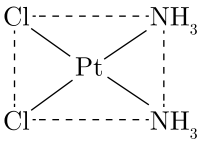
(b) $[Cr(NH_3)_3(H_2O)_3]Cl_3$

49. Draw the geometrical isomers exhibited by the compound $[PtCl_2(NH_3)_2]$.

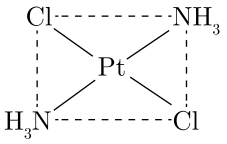
ISC 2010

Ans :

$[PtCl_2(NH_3)_2]$ exists in two geometrical isomers, i.e. cis and trans-forms.



cis-isomer



trans-isomer

50. How does $K_2[PtCl_4]$ get ionised when dissolved in water? Will it form precipitate, when $AgNO_3$ solution is added to it? Give a reason for your answer.

ISC 2017

Ans :

$K_2[Pt\,Cl_4]$ ionise in water as

$$K_2[PtCl_4] \longrightarrow 2K^+ + [PtCl_4]^{2-}$$

The compound does not ionise to give free chloride ions, therefore, it will not form precipitate when $AgNO_3$ solution is added to it.

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Ans :

(a) Linkage isomerism

(b) Hydrate isomerism

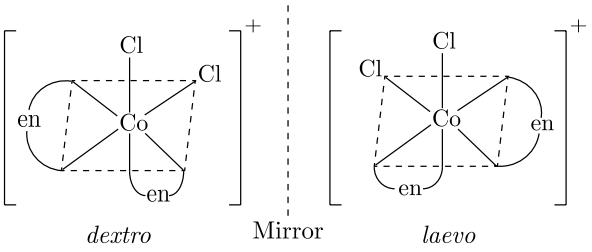
(c) Coordination isomerism

12. Write the structures of optical isomers of the complex ion $[Co(en)_2Cl_2]^+$

Specimen 2018

Ans :

The structure of optical isomers of the complex ion $[Co(en)_2Cl_2]^+$ are shown below.



13. Name the type of isomerism exhibited by the following pairs of compounds.

ISC 2023

(a) $[Co(NH_3)_5(ONO)]Cl_2$ and $[Co(NH_3)_5(NO)_2]Cl_2$

(b) $[Cr(H_2O)_5Cl]Cl_2.H_2O$ and $[Cr(H_2O)_4Cl_2]Cl.2H_2O$

(c) $[Pt(NH_3)_4Cl_2]Br_2$ and $[Pt(NH_3)_4Br_2]Cl_2$

Ans :

(a) In both compounds, ambidentate ligand NO_2 is present in $[Co(NH_3)_5(ONO)Cl_2]$ complex ONO is attached through O with Co while in $[Co(NH_3)_5(NO_2)Cl_2]$ complex NO_2 is attached through N with Co. Hence, they show linkage isomerism.

(b) Given compounds with have different no. of water molecules in coordination sphere which are directly attached to metal ion. Hence, they show hydration isomerism.

(c) Given compounds will give different number of ions in solution, although they have same composition.

Hence, they show ionisation isomerism.

14. For the complex ion of $[Co(NH_3)_6]^{3+}$

(i) state the hybridisation of the complex.

(ii) state the magnetic nature of the complex.

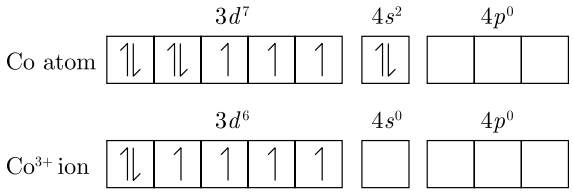
ISC 2014

Ans :

Oxidation number of Co in the complex $[Co(NH_3)_6]^{3+}$ is

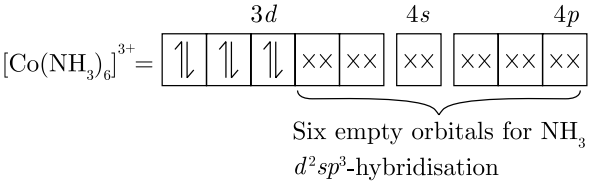
$$x + 6 \times (0) = +3,\ x = +3$$

Electronic configuration of Co is $[Ar]3d^7 4s^2$.



NH_3 is a strong field ligand, it causes pairing of $3d^6$ electrons.

Thus,



(i) Coordination number of the complex is 6. Hence, hybridisation is d^2sp^3.

(ii) All electrons are paired. So, it is diamagnetic.

15. What type of isomers are $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5SO_4]Br$? Give a chemical test to distinguish between the two isomers.

Specimen 2018

Ans :

$[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5SO_4]Br$ shows ionisation isomerism.

Chemical test to distinguish between these two isomers are as follows :

Dissolve both the compounds in water in different test tubes. To the both test tubes,

Test I : Add $BaCl_2$ solution, one compound gives white precipitate indicating the presence of SO_4^{2-} ions. The other compound does not give white precipitate, indicating the absence of SO_4^{2-} a ions.

$$[Co(NH_3)_5Br]SO_4 + BaCl_2(aq) \longrightarrow [Co(NH_3)_5Br]Cl_2 + \underset{\text{White ppt.}}{BaSO_4(s)}\downarrow$$

$$[Co(NH_3)_5SO_4]Br + BaCl_2(aq) \longrightarrow \text{No reaction}$$

Test II : Add $AgNO_3$ solution to both the compounds in separate test tubes.

Only $[Co(NH_3)_5SO_4]Br$ compound gives yellow precipitate, not $[Co(NH_3)_5Br]SO_4$, due to the absence of Br^- as counter ion.

NODIA

Ans :

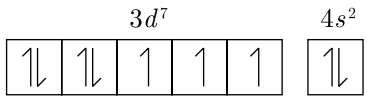
(i) Let the oxidation number of Co in the complex ion $[CoF_6]^{3-}$ is x, then

$$x + 6(-1) = -3$$

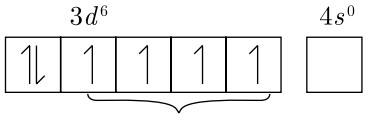
$$x = +3$$

(ii) Electronic configuration of

$$Co = [Ar]3d^7, 4s^2$$

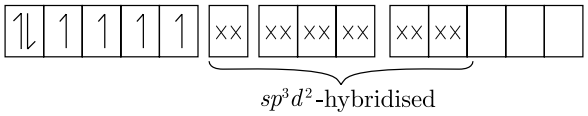
Co atom = 

For $Co^{3+} = [Ar]3d^6, 4s^0$

Co^{3+} ion = 

F^- is a weak filed ligand, thus pairing of electron does not take place.

$[CoF_6]^{3-}$ =



Therefore, there are 4 unpaired electrons.

(iii) As it contains four unpaired electrons, so it is paramagnetic.

(iv) Hexafluoridocobalt (III) ion.

68. of $[Fe(CN)_6]^{3-}$ ion according to the valence bond theory.

ISC 2018, 2015

Ans :

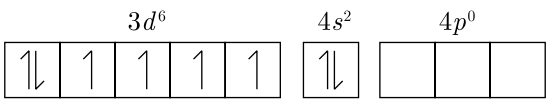
Oxidation number of Fe in the complex, $[Fe(CN)_6]^{3-}$ is

$$x + 6(-1) = -3$$

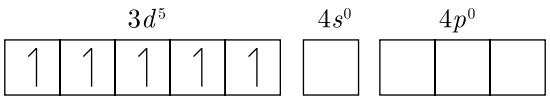
$$x = +3$$

Electronic configuration of Fe is $[Ar]3d^6 4s^2$.

Orbitals of Fe atom

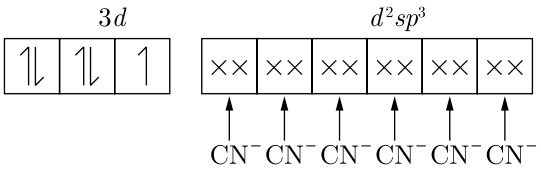


Orbitals of Fe^{3+} ion



CN^- being strong field ligand, paired up the d-electrons of the metal.

Thus, $[Fe(CN)_6]^{3-}$ =



(i) Coordination number of the complex is 6. Hence, hybridisation is d^2sp^3, so geometry is octahedral.

(ii) Since, there is one unpaired electron, so it is paramagnetic.

THREE MARKS QUESTIONS

69. Write the IUPAC names of the following complexes.

ISC 2020

(i) $[Cu(NH_3)_4]SO_4$

(ii) $[Co(en)_2Cl_2]$

(iii) $K_3[Al(C_2O_4)_3]$

Ans :

(i) Tetraamine copper (II) sulphate

(ii) Dichlorobis-(ethane-1, 2-diammine) cobalt(II)

(iii) Potassium trioxalatoaluminate (III)

70. Name the type of isomerism shown by the following pairs of coordination compounds.

(a) $[Pt(H_2O)_4Cl_2]Cl_2.H_2O$ and $[Pt(H_2O)_3Cl_3]Cl.2H_2O$

(b) $[Co(NH_3)_4Cl_2]Br_2$ and $[Co(NH_3)_4Br_4]Cl_2$

(c) $[Cr(H_2O)_5(SCN)]Cl_2$ and $[Cr(H_2O)_5(NCS)]Cl_2$

ISC Specimen 2023

Ans :

(a) Hydrate isomerism

(b) Ionisation isomerism

(c) Linkage isomerism

71. Name of the type of isomerism exhibited by the following pairs of compounds.

ISC 2020

(a) $[Co(ONO)(NH_3)_5]^{2+}$ and $[Co(NO_2)(NH_3)_5]^{2+}$

(b) $[Cr(H_2O)_4Cl_2]Cl.2H_2O$ and $[Cr(H_2O)_5Cl]Cl_2.H_2O$

(c) $[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$

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81. A coordination compound having molecular formula $[Co(NH_3)_4Cl_2]Cl$ exhibits geometrical isomerism. Explain the origin of this isomerism and draw the possible isomeric forms.

ISC 2010

Ans :

The complex possesses octahedral geometry with two chloride ligands coordinated to cobalt.

The chloride ligands may occupy adjacent positions forming cis-isomer or opposite positions forming trans-isomer.

Thus difference in spatial arrangement of ligands around the central metal ion gives rise to geometrical isomerism.

82. Explain why coordination compounds containing ambidentate ligands show linkage isomerism. Give one suitable example.

ISC 2025

Ans :

Ambidentate ligands possess two different donor atoms through which coordination can occur.

Depending upon the donor atom used for bonding, different coordination compounds are formed.

For example, NO_2^- may coordinate through nitrogen forming nitro complex or through oxygen forming nitrito complex, producing linkage isomerism.

83. Explain the significance of Werner's theory in coordination chemistry.

ISC 2002

Ans :

Werner's theory explained the existence of primary and secondary valencies in coordination compounds.

It successfully described ionisation behaviour and spatial arrangement of ligands around the central metal ion.

The theory also explained geometrical isomerism and laid the foundation for modern coordination chemistry.

84. Explain the biological importance of coordination compounds with suitable examples.

ISC 2008

Ans :

Many biologically important molecules are coordination compounds.

Haemoglobin contains iron complex responsible for oxygen transport in blood.

Chlorophyll contains magnesium complex essential for photosynthesis, while vitamin B_{12} contains cobalt coordination compound important for metabolic processes.

85. Differentiate between strong field ligands and weak field ligands on the basis of crystal field splitting and magnetic behaviour of complexes formed.

ISC 2021

Ans :

Strong Field Ligands	**Weak Field Ligands**
Produce large crystal field splitting	Produce small crystal field splitting
Cause pairing of electrons	Do not cause pairing
Form low-spin complexes	Form high-spin complexes
Example: CN-	Example: Cl-

86. A student observed that $K_4[Fe(CN)_6]$ does not give immediate precipitate with $AgNO_3$solution whereas simple potassium chloride does. Explain the observation.

ISC 2010

Ans :

In $K_4[Fe(CN)_6]$, cyanide ions are present inside the coordination sphere and remain bonded to the central metal ion.

Therefore they do not ionise freely in aqueous solution and cannot react immediately with $AgNO_3$.

In potassium chloride, chloride ions are free and readily form precipitate with silver nitrate.

87. Explain optical isomerism in coordination compounds with suitable example.

ISC 2014

Ans :

Optical isomerism arises when coordination compounds form non-superimposable mirror images called enantiomers.

These isomers rotate plane polarised light equally in opposite directions.

For example, $[Co(en)_3]^{3+}$ exhibits optical isomerism because of asymmetric arrangement of three bidentate ligands around cobalt ion.

NODIA

(ii) Given compounds show ionisation isomerism. These type of isomerism are shown by those isomers which have same composition but yield different ions in solution.

58. What type of isomerism is shown by the following coordination compounds?
$[PtCl_2(NH_3)_4]Br_2$ and $[PtBr_2(NH_3)_4]Cl_2$
Write their IUPAC names.

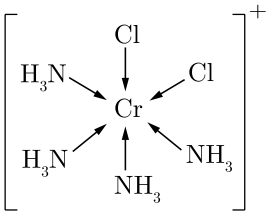
ISC 2018

Ans :
$[PtCl_2(NH_3)_4]Br_2$ and $[PtBr_2(NH_3)_4]Cl_2$ shows ionisation isomerism as both of these compounds will give different type of ions in solution IUPAC names of the given compounds are
$[PtCl_2(NH_3)_4]Br_2$:
Tetraamminedichloroplatinum (IV) bromide
$[PtBr_2(NH_3)_4]Cl_2$:
Tetramminedibromoplatinum (IV) chloride

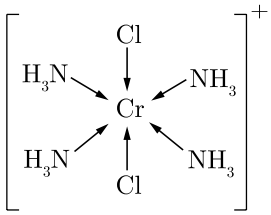
59. Write the IUPAC name of the complex, $[Cr(NH_3)_4Cl_2]^+$.Which type of isomerism will be exhibited by it?

ISC Specimen 2018

Ans :
IUPAC name of complex, $[Cr(NH_3)_4Cl_2]^+$ is tetraamminedichlorochromium (III) ion.
It shows geometrical isomerism as follows:



cis-isomer



trans-isomer

60. Name the type of isomerism shown by the following pair of compounds.

ISC 2014

(i) $[CoCl(H_2O)(NH_3)_4]Cl_2$ and $[CoCl_2(NH_3)_4]Cl.H_2O$

(ii) $[Pt(NH_3)_4][PtCl_6]$ and $[Pt(NH_3)_4Cl_2][PtCl_4]$

Ans :
(i) In both compounds the difference is in the number of water molecule present as ligand (i.e. in coordination sphere) and as molecule of water of crystallisation (i.e. outside the coordination sphere). Hence, they are called hydrate isomers.

(ii) In these compounds, both positive negative ions of salt are complex ions and the two isomers differ in the distribution of ligands in cation and anion. Hence, they are coordination isomers.

61. Name the type of isomerism shown by the following pair of compounds, $[PtCl_2(NH_3)_4]Br_2$ and $[PtBr_2(NH_3)_4]Cl_2$. Give a chemical test to distinguish between the given pair of isomers.

ISC 2010

Ans :
They show ionisation isomerism. It is because both compounds give different ions in solution and have same composition,

$$[PtCl_2(NH_3)_4]Br_2 \xrightleftharpoons{H_2O} [PtCl_2(NH_3)_4]^{2+} + 2Br^-$$

$$[PtBr_2(NH_3)_4]Cl_2 \xrightleftharpoons{H_2O} [PtBr_2(NH_3)_4]^{2+} + 2Cl^-$$

Test When, above compounds are reacted with $AgNO_3$, they give different colour of ppt.

$$[PtCl_2(NH_3)_4]Br_2 + AgNO_3 \longrightarrow \underset{\text{Pale yellow ppt.}}{AgBr}$$

$$[PtBr_2(NH_3)_4]Cl_2 + AgNO_3 \longrightarrow \underset{\text{White ppt.}}{AgCl}$$

62. Name the type of isomerism shown by the following pairs of coordination compounds.

(i) $[Co(NH_3)_5NO_2]Cl_2$ and $[Co(NH_3)_5ONO]Cl_2$

(ii) $[Cr(H_2O)_5Cl]Cl_2.H_2O$ and $[Cr(H_2O)_4Cl_2]Cl.2H_2O$

ISC 2009

Ans :
(i) In both compounds, ambident ligand NO_2 is present. In $[Co(NH_3)NO_2]Cl_2$, NO_2 is coordinated through N and in $[Co(NH_3)_5ONO]Cl_2$, NO_2 is coordinated through O.
Hence, they show linkage isomerism.

(ii) These isomers differ from each other in number of water molecules coordinated to central metal atom, i.e. (Cr). So, they show hydrate isomerism.

63. What type of isomerism is exhibited by the following pairs of compounds?

(a) $[PtCl_2(NH_3)_4]Br_2$ and $[PtBr_2(NH_3)_4]Cl_2$

(b) $[Cr(SCN)(H_2O)_5]^{2+}$ and $[Cr(NCS)(H_2O)_5]^{2+}$

ISC 2017

Ans :
(a) Given compounds will give different ions in solution, although they have same composition.
Hence, they exhibit ionisation isomerism.

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Example: $[Co(NH_3)_4Cl_2]^+$ exists as cis and trans isomers.

The cis isomer has chloride ligands adjacent to each other whereas in trans isomer they occupy opposite positions.

95. Explain why coordination compounds exhibit different colours with different ligands attached to the same metal ion.

ISC 2019

Ans :

Different ligands produce different extents of crystal field splitting in the d-orbitals of the central metal ion.

Electrons absorb specific wavelengths of visible light and undergo d–d transitions.

The colour observed corresponds to the complementary colour of absorbed radiation.

Hence change in ligand changes splitting energy and consequently changes colour of the coordination compound.

96. Explain the formation and significance of coordination compounds in qualitative inorganic analysis.

ISC 2004

Ans :

Many metal ions form coloured coordination complexes with suitable ligands.

These characteristic colours help in identification of metal ions during qualitative analysis.

For example, copper ions form deep blue complex with ammonia.

Silver ions form soluble complex with cyanide ions.

Thus selective complex formation is widely used for detection and separation of metal ions.

97. Explain the significance of ambidentate ligands in coordination chemistry with suitable examples.

ISC 2002

Ans :

Ambidentate ligands possess two different donor atoms through which bonding with metal ion can occur.

They produce linkage isomerism in coordination compounds.

Example:

NO_2^- may coordinate through nitrogen forming nitro complex or through oxygen forming nitrito complex.

Similarly SCN^- may coordinate through sulphur or nitrogen atom.

These ligands increase structural diversity in coordination chemistry.

98. Explain why tetrahedral complexes generally show lower crystal field splitting energy than octahedral complexes.

ISC 2017

Ans :

In tetrahedral complexes, ligands approach between the coordinate axes where electron density of d-orbitals is lower.

Consequently electrostatic repulsion between ligand electrons and d-electrons decreases.

Therefore splitting of d-orbitals becomes smaller compared to octahedral complexes where ligands approach directly along the axes.

Hence tetrahedral complexes usually possess lower crystal field splitting energy.

99. Explain Werner's coordination theory. Mention any two important postulates and one limitation.

ISC 2025

Ans :

Werner proposed that metals possess two types of valencies:

primary valencies and secondary valencies.

Primary valencies correspond to oxidation state and are ionisable.

Secondary valencies correspond to coordination number and are non-ionisable and directional.

The theory explained geometries and isomerism in coordination compounds successfully.

Limitation:

Werner's theory could not explain magnetic properties and colour of coordination compounds.

100. Explain the formation, geometry, hybridisation and magnetic behaviour of the complexes:

ISC 2021

(i) $[Ni(CN)_4]^{2-}$

(ii) $[NiCl_4]^{2-}$

Ans :

(i) In $[Ni(CN)_4]^{2-}$, cyanide ion acts as a strong field ligand and causes pairing of d-electrons. The complex undergoes dsp^2 hybridisation and acquires square planar geometry.
All electrons become paired, therefore the complex is diamagnetic.

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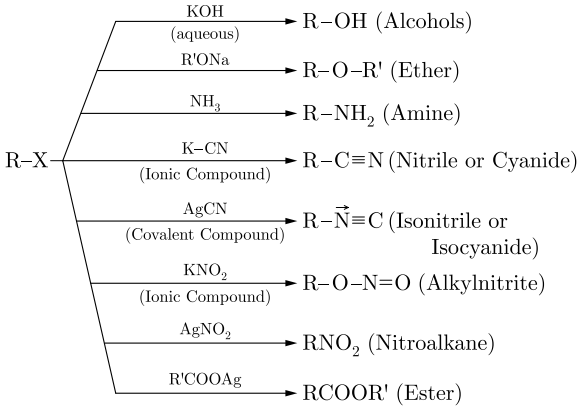
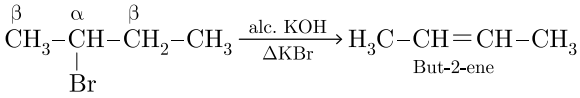
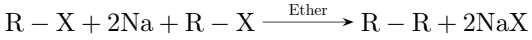


6.2 Elimination Reaction

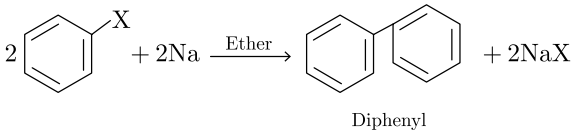


Saytzeff's Rule : When an alkyl halide is treated with alcoholic KOH it undergoes dehydrohalogenation reaction to give a product having more alkylated double bond.

6.3 Wurtz's Reaction

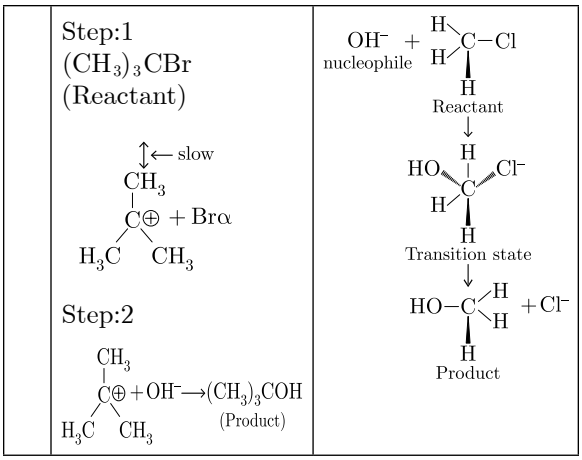


6.4 Fitting Reaction

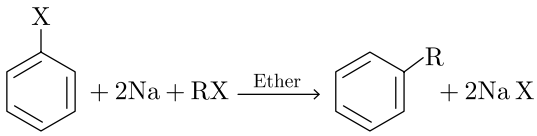


6.5 Mechanism of Nucleophilic Substitution Reactions

	S_N^1	S_N^2
1.	Nucleophilic substitution is uni-molecular.	Nucleophilic substitution is bimolecular.
2.	It takes place in two steps.	It takes place in one step.
3.	They are first order reactions.	They are mostly second order reactions.
4.	It leads to racemisation.	It leads to inversion of configuration.



6.6 Wurtz-Fitting Reaction



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7. POLYHALOGEN COMPOUNDS

Carbon compounds containing more than one halogen atom are usually referred to as polyhalogen compounds.

7.1 Dichloromethane

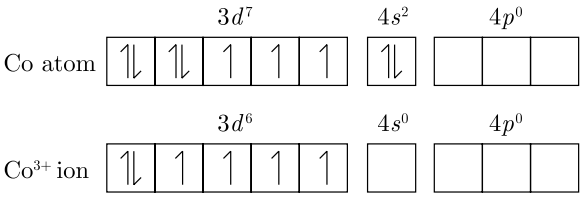
Applications

1. Widely used as a solvent as a paint remover and as a processing solvent in the manufacture of drugs.
2. It is also used in metal cleaning and as a finishing solvent.

Harmful Effects of Dichloromethane

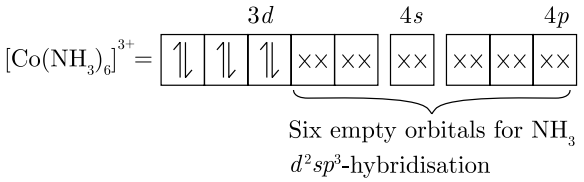
1. Methylene chloride can severely harm the human central nervous system.
2. Exposure to lower level of methylene chloride in air can lead to slightly impaired hearing and vision.
3. Higher level of methylene chloride in air causes dizziness, nausea, tingling and numbness in fingers and toes.
4. In humans, direct skin contact with methylene chloride causes intense burning and mild redness of the skin, direct contact with eyes can also burn the cornea.

(iii) Electronic configuration of Co is $[Ar]3d^7 4s^2$.



NH_3 is a strong field ligand, it causes pairing of $3d^6$ electrons.

Thus,



Thus, hybridisation of $[Co(NH_3)_6]^{3+}$ is d^2sp^3.

(iv) As all electrons are paired so, it is diamagnetic.

105. Using the valence bond approach, predict the shape, hybridisation and magnetic behaviour of $[Ni(CO)_4]$. (Atomic number of Ni =28)

ISC 2020

Ans :

It was developed by Llnus Pauling. In brief,

(a) Central atom/ion makes available required number of empty orbitals.

(b) These orbitals undergo hybridisation to give same number of hybrid orbitals of equal energy.

(c) These hybridised orbitals are allowed to overlap with ligand orbitals that can donate electron pairs for bonding, and form strong ligand-metal coordinate covalent bonds.

Hybridisation and geometry of complexes

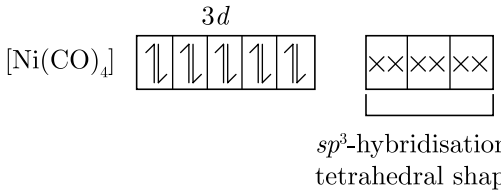
Coordination number	Type of hybridisation	Geometry of the complex formed
2	sp	Linear
3	sp^2	Trigonal planar
4	sp^3	Tetrahedral
4	dsp^2	Square planar
5	dsp^3, sp^3d	Trigonal bipyramidal
6	sp^3d^2, d^2sp^3	Octahedral

(d) Ligands must have one sigma orbital containing lone pair of electrons.

(e) During complex formation, the Hund's rule of maximum multiplicity is followed while, in case of strong ligands, unpaired electrons get paired.

(f) A complex is paramagnetic if it contains unpaired electrons. If all the electrons are paired, the complex is diamagnetic in nature.

(g) The outer orbital (high spin) or inn€r orbital (low spin) complexes are formed depending whether outer d-orbitals or inner d-orbitals of metol ion are used, Using VBT, formation of $[Ni(CO)_4]$ can be represented as



It is diamagnetic as all the electrons are paired.

CASE BASED QUESTIONS

106. A cobalt complex containing ethylenediamine ligands was found and showed optical activity. The complex existed in two forms which rotated plane polarised light in opposite directions.

(i) Name the type of isomerism shown by the complex $[Co(en)_3]^{3+}$.

(ii) What is the denticity of ethylenediamine ligand?

(iii) Explain why the complex exhibits optical activity although both forms possess the same molecular formula.

Ans :

(i) Optical isomerism.

(ii) Ethylenediamine is a bidentate ligand.

(iii) The complex possesses asymmetric arrangement of three bidentate ligands around cobalt ion. Consequently two non-superimposable mirror images called enantiomers are formed. These isomers rotate plane polarised light equally in opposite directions and therefore exhibit optical activity.

107. A student added ammonia solution gradually to copper sulphate solution. Initially a light blue precipitate formed which dissolved in excess ammonia producing a deep blue solution.

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(ii) In $[NiCl_4]^{2-}$, chloride ion is a weak field ligand and does not cause pairing.
The complex undergoes sp^3 hybridisation and possesses tetrahedral geometry.
Presence of unpaired electrons makes the complex paramagnetic.

101. A coordination compound having molecular formula $[Co(NH_3)_5Br]SO_4$ gives white precipitate with $BaCl_2$ solution but does not give precipitate with $AgNO_3$. Explain the observation and identify the type of isomerism shown by its isomeric form $[Co(NH_3)_5SO_4]Br$.

ISC 2023

Ans :

In $[Co(NH_3)_5Br]SO_4$, sulphate ion is present outside the coordination sphere and therefore reacts with $BaCl_2$ to produce white precipitate of $BaSO_4$.

Bromide ion is present inside the coordination sphere and hence does not react with $AgNO_3$.

Its isomeric form $[Co(NH_3)_5SO_4]Br$ contains bromide ion outside the coordination sphere.

Such exchange between ligand and counter ion gives rise to ionisation isomerism.

102. Explain optical isomerism in coordination compounds with suitable example. Why do optical isomers differ in behaviour towards plane polarised light?

ISC 2018

Ans :

Optical isomerism arises when coordination compounds exist as non-superimposable mirror images called enantiomers.

Example: $[Co(en)_3]^{3+}$ shows optical isomerism due to asymmetric arrangement of three bidentate ligands around cobalt ion.

One isomer rotates plane polarised light towards right and is called dextrorotatory.

The other rotates plane polarised light towards left and is called levorotatory.

This difference arises because the spatial arrangement of ligands in the two forms is different.

103. Consider the complex ion $[Co(CN)_6]^{3-}$ and answer the following questions.

(Atomic number of Co = 27)

(a) Type of hybridisation of central metal atom.

(b) Magnetic nature.

(c) Geometry of the complex ion.

(d) Low spin complex or high spin complex.

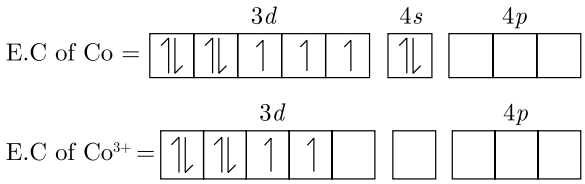
ISC Specimen 2023

Ans :

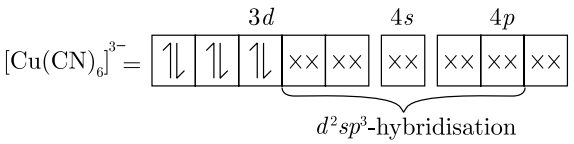
(a) Electronic configuration for

$$_{27}Co \longrightarrow [Ar]3d^7 4s^2$$

Oxidation state of Co in $[Co(CN)_6]^{3-} = +3$



Since, CN^- is a strong ligand, it will pair up electron to form low spin complex.



Hence, $[Cu(CN)_6]^{3-}$ is d^2sp^3 hybridised.

(b) Since, all electrons are paired, so it is diamagnetic in nature.

(c) The geometry of $[Cu(CN)_6]^{3-}$ is octahedral

(d) It form low spin complex as CN^- is a strong field ligand, so it will pair up the electrons.

104. For the coordination complex ion $[Co(NH_3)_6]^{3+}$

(i) Give the IUPAC name of the complex ion.

(ii) What is the oxidation number of cobalt in the complex ion?

(iii) State the type of hybridisation of the complex ion.

(iv) State the magnetic behaviour of the complex ion.

ISC 2017

Ans :

(i) Hexaamminecobalt (III) ion.

(ii) Let the oxidation number of Co in the complex $[Co(NH_3)_6]^{3+}$ be x.

$$x + 6 \times (0) = +3$$
$$x = +3$$

NODIA

(iii) Explain why EDTA forms highly stable complexes with metal ions.

Ans :

(i) EDTA is a hexadentate ligand.

(ii) Chelate complexes.

(iii) EDTA forms multiple coordinate bonds simultaneously with the same metal ion and produces stable ring structures called chelates. Breaking all these bonds together becomes difficult, therefore EDTA complexes possess very high stability.

113. A student observed that different chromium coordination compounds exhibited different colours although chromium remained the same central metal ion.

ISC 2015

(i) Which theory explains colour in coordination compounds?

(ii) Which orbitals are involved in colour production?

(iii) Explain why different ligands produce different colours with the same metal ion.

Ans :

(i) Crystal field theory.

(ii) d-orbitals.

(iii) Different ligands produce different extents of crystal field splitting in the d-orbitals of the metal ion. Electrons absorb different wavelengths of visible light for d–d transitions. Consequently complexes containing different ligands exhibit different colours.

114. A coordination compound having formula $[Co(NH_3)_5Cl]SO_4$ was analysed in the laboratory. The compound produced white precipitate with $BaCl_2$ solution but failed to give precipitate with $AgNO_3$. The teacher explained that the behaviour depends upon the ions present inside and outside the coordination sphere.

(i) Which ion is present outside the coordination sphere in the complex?

(ii) Why does the compound fail to give precipitate with $AgNO_3$ solution?

(iii) Name and explain the type of isomerism shown by its isomeric form $[Co(NH_3)_5SO_4]Cl$

Ans :

(i) SO_4^{2-} ion is present outside the coordination sphere.

(ii) Chloride ion is coordinated directly to cobalt inside the coordination sphere and therefore does not ionise freely in solution to react with $AgNO_3$.

(iii) The compounds show ionisation isomerism. In this type of isomerism, exchange occurs between ligand present inside the coordination sphere and counter ion present outside the coordination sphere, producing compounds with different ionic behaviour in solution.

115. A student prepared two nickel complexes, $[Ni(CN)_4]^{2-}$ and $[NiCl_4]^{2-}$. One complex was found to be square planar and diamagnetic whereas the other was tetrahedral and paramagnetic.

(i) Which complex possesses square planar geometry?

(ii) Which ligand behaves as a strong field ligand in the above complexes?

(iii) Explain the difference in geometry and magnetic behaviour of the two complexes using crystal field theory.

Ans :

(i) $[Ni(CN)_4]^{2-}$ possesses square planar geometry.

(ii) CN^- behaves as a strong field ligand.

(iii) Cyanide ion produces large crystal field splitting energy and causes pairing of d-electrons, resulting in dsp^2 hybridisation, square planar geometry and diamagnetic behaviour. Chloride ion is a weak field ligand and does not cause pairing, therefore sp^3 hybridisation, tetrahedral geometry and paramagnetic behaviour are observed.

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(i) Name the complex ion responsible for the deep blue colour.
(ii) Which type of electronic transition produces colour in the complex?
(iii) Explain the role of ligands in producing colour in coordination compounds.

Ans :
(i) $[Cu(NH_3)_4]^{2+}$ complex ion.
(ii) d–d electronic transition.
(iii) Ligands surrounding the central metal ion produce crystal field splitting of d-orbitals into different energy levels. Electrons absorb visible light and undergo transitions between these levels. The wavelength absorbed determines the colour observed in the coordination compound.

108. Two iron complexes, $[Fe(CN)_6]^{4-}$ and $[FeF_6]^{4-}$, showed different magnetic behaviour although iron existed in the same oxidation state in both compounds.
(i) Which complex is diamagnetic?
(ii) Which ligand belongs to weak field category?
(iii) Explain the difference in magnetic behaviour of the two complexes using crystal field theory.

Ans :
(i) $[Fe(CN)_6]^{4-}$ is diamagnetic.
(ii) Fluoride ion is a weak field ligand.
(iii) Cyanide ion produces large crystal field splitting and causes pairing of electrons, making the complex diamagnetic. Fluoride ion produces small splitting energy and therefore electrons remain unpaired, resulting in paramagnetic behaviour of the complex.

109. A platinum complex $[Pt(NH_3)_2Cl_2]$ was studied in medicinal chemistry. One geometrical isomer showed anticancer properties while the other remained biologically inactive.
(i) Which geometrical isomer acts as an anticancer drug?
(ii) Which type of isomerism is shown by the complex?
(iii) Explain why the two isomers exhibit different biological behaviour.

Ans :
(i) Cis-isomer acts as anticancer drug.
(ii) Geometrical isomerism.
(iii) The two isomers differ in spatial arrangement of ligands around platinum ion. This difference changes interaction with biological molecules inside cells. Therefore cis-platin exhibits anticancer activity whereas trans-platin does not show similar therapeutic effect.

110. During qualitative analysis, a student observed that potassium ferrocyanide does not immediately give free cyanide ions in aqueous solution although cyanide ions are present in the compound.
(i) Write the formula of potassium ferrocyanide.
(ii) Why are cyanide ions not freely available in solution?
(iii) Explain the significance of coordination sphere in coordination compounds.

Ans :
(i) $K_4[Fe(CN)_6]$
(ii) Cyanide ions are bonded directly to iron inside the coordination sphere.
(iii) The coordination sphere contains ligands directly attached to the central metal ion through coordinate bonds. Ions present inside the coordination sphere do not ionise freely in aqueous solution and therefore exhibit behaviour different from ordinary ionic compounds.

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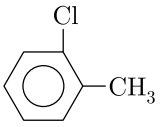
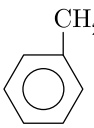
111. A student compared octahedral and tetrahedral complexes and found that tetrahedral complexes generally possess smaller crystal field splitting energy.
(i) Along which direction do ligands approach in octahedral complexes?
(ii) Which type of complexes generally possess larger crystal field splitting energy?
(iii) Explain why tetrahedral complexes show smaller splitting energy than octahedral complexes.

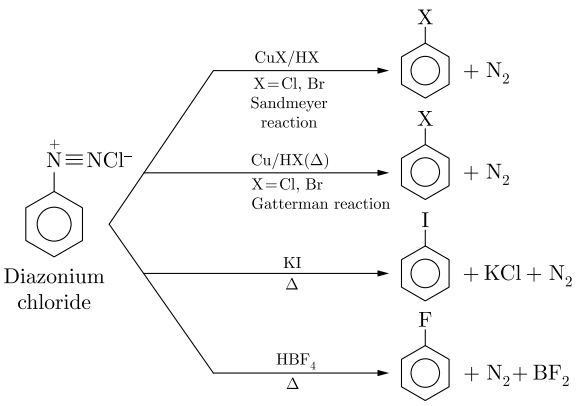
Ans :
(i) Ligands approach along the coordinate axes.
(ii) Octahedral complexes.
(iii) In tetrahedral complexes, ligands approach between the coordinate axes where electron density of d-orbitals is lower. Consequently repulsion between ligand electrons and d-electrons decreases, resulting in smaller crystal field splitting energy.

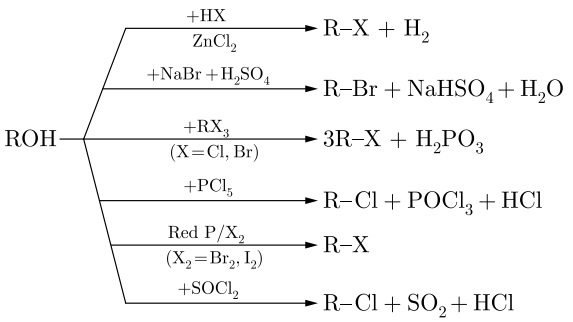
112. EDTA is extensively used in complexometric titrations and water hardness estimation because of its strong complex forming ability.
(i) What is the denticity of EDTA ligand?
(ii) What type of complexes are formed by EDTA?

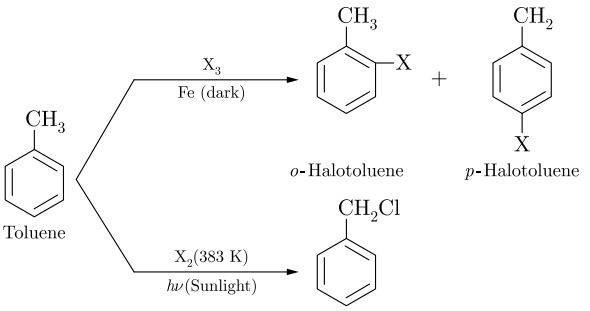
Nomenclature		
Structure	**Common Name**	**IUPAC Name**
$CH_3CH_2CH(Cl)CH_3$	Sec-Butyl chloride	2-Chlorobutane
$(CH_3)_3CCH_2Br$	Neo-Pentyl bromide	1-Bromo-2, 2-dimethyl propane
$(CH_3)_3CBr$	Tert-Butyl bromide	2-Bromo -2-methyl propane
CH_2-CHCl	Vinyl chloride	Chloroethane
CH_2-CHCH_2Br	Allyl bromide	3-Bromo propene
	o-Chlorotoluene	1-chloro-2-methylbenzene
	Benzyl chloride	α-Chlorotoluene/ Chloromethyl benzene

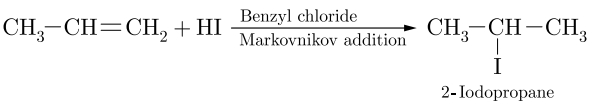
4. PREPARATION OF HALOALKANES AND HALOARENES

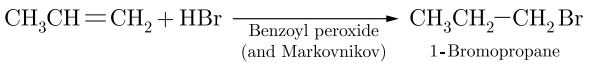
Preparation of haloalkanes and haloarenes are shown below :



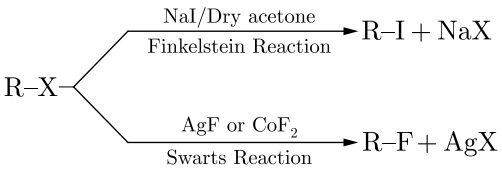








5. IMPORTANT NAME REACTIONS USED FOR THE PREPARATION OF HALOGENS



Racemic Mixture

A mixture of equal amount of two enantiomers is called racemic mixture (d and l).

Racemisation

The process of conversion of one enantiomer (+ or −) into a racemic mixture is called racemisation.

Retention of Configuration

Preservation of the spatial arrangements of bond at an asymmetric centre during a chemical reaction.

6. CHEMICAL PROPERTIES

6.1 Nucleophilic Substitution in Haloalkanes (Important Reactions)

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2. The gas obtained on heating iodoform with silver powder is

ISC Specimen 2021-22 (Sem-1)

(a) propane (b) ethane

(c) ethyne (d) ethene

Ans : (c) ethyne

When iodoform is heated with silver powder, acetylene is formed.

$$2CHI_3 + 6Ag \longrightarrow \underset{\text{Ethyne (acetylene)}}{CH \equiv CH}$$

3. During the course of S_N1 reaction, the intermediate species formed is

ISC Specimen 2021-22 (Sem-1), 2018

(a) a carbocation

(b) a free radical

(c) a carbanion

(d) an intermediate complex

Ans : (a) a carbocation

Carbocation During S_N1 reaction, a carbocation is formed as an intermediate species. For example, in S_N1 reaction between *tert*-butyl bromide and hydroxide ion forms, carbocation intermediate.

4. The optically active compound is

ISC Specimen 2021-22 (Sem-1)

(a) butan-l-ol

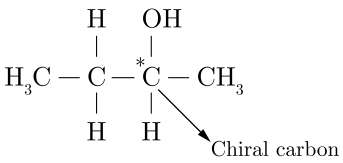
(b) butan-2-ol

(c) propan-1-ol

(d) 2-methylpropan-1-ol

Ans : (b) butan-2-ol

Butan-2-ol is optically active compound due to the presence of a chiral carbon.



5. Which among the following reacts fastest by S_N2 reaction?

ISC Specimen 2018

(a) $(CH_3)_3C - Br$ (b) $(CH_3)_2CHBr$

(c) $CH_3 - CH_2 - Br$ (d) $CH_3 - Br$

Ans : (d) $CH_3 - Br$

The order of reactivity of alkyl halides towards $S_N2$reaction is as follows :

Methyl halide > Primary halide > Secondary halide > Tertiary halide

Therefore, among the given options, CH_3Br reacts fastest by S_N2 reaction.

6. Which polyhalogen compound was earlier widely used as an antiseptic?

ISC 2023

(a) Carbon tetrachloride

(b) Dichloromethane

(c) Iodoform

(d) Freon-12

Ans : (c) Iodoform

Iodoform or triiodomethane is a yellow crystalline compound possessing antiseptic properties due to slow liberation of iodine. It was widely used for dressing wounds and preventing infections. However, because of its unpleasant smell and availability of better antiseptics, its medical use has decreased considerably in modern times.

7. During hydrolysis of optically active 2-bromobutane, the product obtained was optically inactive due to formation of equal amounts of two enantiomers. Which mechanism is responsible for this observation?

ISC 2020

(a) Free radical substitution

(b) S_N2 mechanism

(c) Elimination mechanism

(d) S_N1 mechanism

Ans : (d) S_N1 mechanism

In the S_N1 mechanism, the leaving group first departs to form a planar carbocation intermediate. Since the carbocation is planar, the nucleophile can attack from either side with equal probability. Consequently both enantiomers are formed in equal amounts, producing a racemic mixture which becomes optically inactive.

8. Which of the following haloalkanes undergoes nucleophilic substitution through the fastest S_N2 mechanism?

ISC 2016

(a) Tert-butyl bromide

(b) Ethyl bromide

(c) Methyl bromide

(d) Neo-pentyl bromide

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7.2 Trichloromethane (Chloroform)

Applications of Trichloromethane are as follows:

1. Chloroform is employed as a solvent for fats, alkaloids and other substances.
2. In the production of refrigerant, freon R-22.

Harmful Effects of Chloroform

1. Breathing of even about 900 parts of chloroform per million parts of air for a short period of time can cause dizziness, fatigue and headache.
2. Chronic chloroform exposure may cause damage to the liver and kidneys.
3. Chloroform is slowly oxidised by air in the presence of light to an extremely poisonous gas named carbonyl chloride, also known as phosgene. It is therefore stored in closed dark coloured bottles completely filled so that air can be kept out.

7.3 Tri-iodomethane (Iodoform)

A yellow volatile solid sweet smelling haloform, made by the haloform reaction.

Application

It was earlier used as an antiseptic. Due to its objectionable smell, it has been replaced by other formulations containing iodine.

7.4 Tetrachloromethane (Carbon tetrachloride), CCl_4

A colourless volatile liquid with a characteristic colour, virtually soluble in water but it is miscible with many organic liquids, such as ethanol and benzene.

Applications

1. Used in the manufacture of refrigerants and propellants, for example aerosol.
2. In the synthesis of chlorofluorocarbons and other chemicals.
3. It is widely used as a cleaning fluid.
4. It is also used as a fire extinguisher.

Harmful Effects of CCl_4

1. Most common effects are dizziness, slight headache, nausea and vomiting, which an even cause permanent damage to the nerve cells.
2. Exposure to CCl_4 can make the heart beat irregular or even stops it.
3. When CCl_4 is released into the air, it rises upto the atmosphere and depletes the ozone layer. Depletion of ozone layer is believed to increase the human exposure to ultraviolet rays, leading to increased skin cancer, eye diseases and disorder.

7.5 Freons (CCL_2F_2)

The chlorofluorocarbon compounds of methane and ethane are collectively known as freons.

Properties

1. They are extremely stable, unreactive, non-toxis, non-corrosive and easily liquefiable gases.
2. Freon-12 (CCl_2F_2) is one of the most common freons in industrial use.
3. It is prepared by the action of antimony fluoride on carbon tetrachloride in the presence of antimony pentachloride.
4. In stratosphere, freon is able to initiate the radical chain reactions that can upset the natural ozone balance.

NODIA

7.6 p, p' - Dichloro Diphenyl Trichloroethane (DDT)

1. It is the first chlorinated organic insecticide.
2. DDT is not metabolised very rapidly by animals, instead it is deposited and stored in the fatty tissues.
3. It is manufactures by heating a mixture of chloral and chlorobenzene in the presence of concentrated sulphuric acid.

****

OBJECTIVE QUESTIONS

1. The reaction of chlorine with methane is a _____reaction which involves _____ fission of the C—H bond.

ISC 2007, 2000

Ans :

The reaction of chlorine with methane is a substitution reaction which involves homolytic fission of the C—H bond.

$$CH_4 + Cl_2 \xrightarrow{\text{Sunlight}} CH_3Cl + HCl$$

H-atom is substituted by Cl-atom. It follows free radical mechanism.

CHAPTER 6

Haloalkanes and Haloarenes

SUMMARY

1. ALKYL HALIDES OR HALOALKANES

Organic compounds in which one or more hydrogen atom of an alkane have been substituted by a halogen atom. For example, chloromethane, CH_3Cl, dibromoethane, CH_2BrCH_2Br, etc. Haloalkanes can be formed by direct reaction between alkanes and halogens using ultraviolet radiation. They are usually prepared by the reaction of an alcohol with a halogen carrier.

2. REACTIONS OF HALOALKANES INVOLVE

1. Nucleophilic substitution
2. Elimination reaction
3. Reaction with metals

2.1 Nucleophilic Substitution Reactions

Nucleophilic substitution reactions are categorised as S_N^1 and S_N^2 on the basis of kinetic properties.

A S_N^2 reaction proceeds with stereo-chemical inversion while a S_N^1 reaction proceeds with racemisation.

2.2 Key Terms in Optical Isomerism

Optical isomerism arises in molecules that are non-superimposable on their mirror images. Such molecules are said to be chiral and the property is called chirality. The following are the important terms related to optical isomerism that are frequently encountered in the study of haloalkanes and their reactions.

1. **Optically Active Molecule : It is a molecule that cannot be superimposed on its mirror image. It is also called chiral molecule.**

2. **Asymmetric Carbon :** It is the carbon atom that is bonded to four different groups. It is also called chiral carbon.

3. **Enantiomers :** These are optical isomers that are mirror images of each other.

4. **Diastereoisomers :** These are optical isomers that are not mirror images of each other.

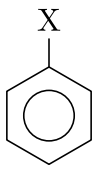
3. FORMATION OF HALOALKANES

Halogen derivatives of organic compounds are classified on the basis of the type of carbon to which the halogen is attached.

$$RH + X_2 \longrightarrow R - X + HX$$

The following are the two broad categories :

1. Haloalkanes : Halogen derivatives of alkanes are called haloalkanes. For e.g., $X - CH_3$.
2. Haloarenes : Halogen derivatives of arenes are called haloarenes.
   E.g. $X - C_6H_5$.



3.1 Types of Dihalides :

When two halogen atoms are present in a haloalkane molecule, the compound is called a dihalide. Dihalides are further classified into two types on the basis of the position of the halogen atoms :

(i) **Vicinal Dihalides :** Halogen derivatives where the two halogen atoms are attached on the adjacent carbon atom.

E.g., CH_2Cl / CH_2Cl

(ii) **Geminal Dihalide :** Where the two halogen atoms are attached to the same carbon atom. For e.g., CH_3CHBr_2.

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Ans : (c) Methyl bromide

S_N2 reactions proceed through backside attack by the nucleophile. Steric hindrance around the carbon atom greatly affects the reaction rate. Methyl bromide has the least steric hindrance because the carbon atom is attached only to hydrogen atoms. Therefore nucleophilic attack occurs most easily and rapidly in methyl bromide.

9. In the reaction of 2-bromobutane with alcoholic KOH, the major product formed is but-2-ene. This observation is explained by:

ISC 2024

(a) Markovnikov's rule

(b) Saytzeff's rule

(c) Anti-Markovnikov's rule

(d) Hoffmann rule

Ans : (b) Saytzeff's rule

According to Saytzeff's rule, during dehydrohalogenation the major alkene formed is the more substituted and more stable alkene. In the elimination of hydrogen bromide from 2-bromobutane, but-2-ene contains a more substituted double bond compared to but-1-ene, hence it becomes the predominant product formed during the reaction.

10. Which of the following compounds contains a chiral carbon atom?

ISC 2021

(a) 2-Chlorobutane

(b) Chloromethane

(c) 2-Chloropropane

(d) Neopentyl chloride

Ans : (a) 2-Chlorobutane

A chiral or asymmetric carbon atom is attached to four different groups. In 2-chlorobutane, the second carbon is attached to hydrogen, chlorine, methyl and ethyl groups, all of which are different. Therefore the molecule becomes optically active and can exist in two enantiomeric forms.

11. Haloarenes are less reactive towards nucleophilic substitution reactions mainly because:

ISC 2025

(a) Halogen atoms are strongly electronegative

(b) Carbon-halogen bond acquires partial double bond character

(c) Haloarenes are insoluble in water

(d) Benzene ring contains six carbon atoms

Ans : (b) Carbon-halogen bond acquires partial double bond character

In haloarenes, resonance occurs between the lone pair electrons of the halogen atom and the benzene ring. This delocalisation imparts partial double bond character to the carbon-halogen bond, making it shorter and stronger than the corresponding bond in haloalkanes. Consequently haloarenes resist nucleophilic substitution reactions significantly more strongly.

12. Which of the following compounds is a vicinal dihalide?

ISC 2011

(a) CH_3CHCl_2

(b) $CH_2Cl - CH_2Cl$

(c) $CHCl_3$

(d) CCl_4

Ans : (b) $CH_2Cl - CH_2Cl$

Vicinal dihalides contain two halogen atoms attached to adjacent carbon atoms. In $CH_2Cl - CH_2Cl$, each chlorine atom is attached to neighbouring carbon atoms, satisfying the definition of vicinal dihalide. Such compounds are commonly formed by addition of halogens across the double bond of alkenes.

13. Which of the following statements correctly explains racemisation?

ISC 2010

(a) Formation of only one enantiomer

(b) Conversion of alkene into alkane

(c) Formation of equal amounts of two enantiomers

(d) Removal of halogen atom from haloalkane

Ans : (c) Formation of equal amounts of two enantiomers

Racemisation is the process in which an optically active compound converts into an equimolar mixture of two enantiomers. Since the two enantiomers rotate plane polarised light equally in opposite directions, their optical activities cancel each other completely and the resulting racemic mixture becomes optically inactive overall.

NODIA

Ans : (d)

$$\underset{\text{Silver acetate}}{CH_3COO^-Ag^+} + Br_2 \xrightarrow{CCl_4} \underset{\text{Bromomethane}}{CH_3Br} + \underset{\text{Carbon dioxide}}{CO_2\uparrow} + \underset{\text{Silver bromide}}{AgBr\downarrow}$$

(ii) What is the above reaction known as?

(a) Finkelstein reaction

(b) Swarts reaction

(c) Hunsdiecker reaction

(d) Sandmeyer's reaction

Ans : (c)

This reaction is known as Borodine-Hunsdiecker reaction.

37. The product formed when aniline is warmed with chloroform and caustic potash.

ISC 2010, 2002

(a) Phenyl chloride

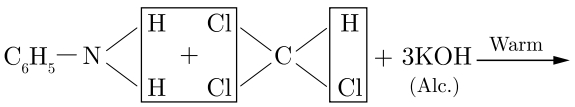
(b) Methyl isocyanide

(c) Phenyl isocyanide

(d) Nitrophenol

Ans : (c) Phenyl isocyanide

Phenyl isocyanide In carbylamine reaction, when chloroform is warmed with aniline and alcoholic caustic potash, phenyl isocyanide is obtained which has an extremely offensive smell.



$$C_6H_5-N\equiv C + 3KCl + 3H_2O$$

Phenyl isocyanide

38. Ethyl alcohol when reacts with PCl_5 gives a compound (A). When compound (A) is treated with alc. KOH, compound (B) is formed alongwith KCl and H_2O.

(i) The compound (A) is

ISC 2021-22 (Sem I)

(a) $C_2H_4Cl_2$ (b) CH_3CHO

(c) C_2H_5Cl (d) CH_3OH

(ii) The compound (B) is

(a) C_2H_2 (b) C_2H_4

(c) C_2H_6 (d) C_2H_5OH

Ans :

When ethyl alcohol reacts with PCl_5, it forms ethyl chloride.

(i) (c)

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH} + PCl_5 \longrightarrow \underset{\substack{\text{(Ethyl chloride)}\\(A)}}{C_2H_5Cl} + POCl_3 + HCl$$

(ii) (b) When ethyl chloride reacts with alc KOH undergoes β-elimination reaction to form ethene as a product.

$$\underset{(A)}{C_2H_5Cl} \longrightarrow \underset{(B)}{C_2H_4}$$

39. The reaction $CH_3Br + OH^- \longrightarrow CH_3OH + Br^-$

(i) The expected mechanism of the above reaction is

ISC Specimen 2021-22 (Sem-I)

(a) S_N1 mechanism (b) S_N2 mechanism

(c) S_E1 mechanism (d) S_E2 mechanism

(ii) The above reaction is

(a) elimination reaction

(b) nucleophilic addition reaction

(c) nucleophilic substitution reaction

(d) electrophilic substitution reaction

Ans :

(i) (b) S_N2 mechanism

Reason Since the given alkyl halide (CH_3Br) is a primary alkyl halide which usually undergoes substitution by S_N2 mechanism.

(ii) (c) $CH_3Br + OH^- \longrightarrow CH_3OH + Br^-$ is a nucleophilic reaction.

In this reaction, the nucleophile (OH^-) attacks on the positively charged carbon of haloalkane and the halogen leaves the group.

40. **Assertion (A)** Nitration of chlorobenzene leads to the formation of *m*-nitrochlorobenzene.

Reason (R) Nitro ($-NO_2$) group is *m*-directing group.

ISC Specimen 2021

(a) Both (A) and (R) are correct and (R) is the correct explanation of (A).

(b) Both (A) and (R) are correct but (R) is not the correct explanation of (A).

(c) (A) is correct and (R) is incorrect.

(d) (A) is incorrect and (R) is correct.

Ans : (d) (A) is incorrect and (R) is correct.

Assertion is incorrect but Reason is correct as the chlorination of nitrobenzene. (not the

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Freons or chlorofluorocarbons are chemically stable compounds that reach the stratosphere without decomposition. Ultraviolet radiation breaks them releasing chlorine radicals. These radicals initiate chain reactions that destroy ozone molecules repeatedly. Ozone depletion increases penetration of harmful ultraviolet radiation, causing skin cancer, eye disorders and ecological damage.

20. In the S_N2 mechanism, the reaction rate depends upon:

ISC 2023

(a) Concentration of alkyl halide only

(b) Concentration of nucleophile only

(c) Concentration of solvent only

(d) Concentration of both alkyl halide and nucleophile

Ans : (d) Concentration of both alkyl halide and nucleophile

S_N2 reactions are bimolecular nucleophilic substitution reactions occurring in a single step. The rate determining step involves simultaneous participation of both the alkyl halide and nucleophile. Hence the reaction rate depends upon the concentration of both reactants, making it a second order reaction overall.

21. Which of the following reactions is used for preparation of biaryl compounds?

ISC 2024

(a) Wurtz reaction

(b) Fittig reaction

(c) Sandmeyer reaction

(d) Kolbe reaction

Ans : (b) Fittig reaction

Fittig reaction involves the reaction of aryl halides with sodium metal in dry ether. Two aryl groups combine together producing biaryl compounds such as biphenyl. This reaction is analogous to the Wurtz reaction, but instead of alkyl groups, aromatic rings participate in carbon-carbon bond formation.

22. Carbon tetrachloride was once widely used in fire extinguishers because it:

ISC 2011

(a) Is highly combustible

(b) Produces oxygen on heating

(c) Is non-flammable and volatile

(d) Reacts vigorously with water

NODIA

Ans : (c) Is non-flammable and volatile

Carbon tetrachloride is a non-flammable volatile liquid capable of suppressing combustion effectively. Its vapours isolate oxygen from the burning material and help extinguish fire. Because of its toxic effects on the nervous system and harmful environmental impact including ozone depletion, its use has been significantly restricted today.

23. Which of the following compounds is classified as a geminal dihalide?

ISC 2025

(a) $CH_2Br - CH_2Br$

(b) $CH_3 - CHCl_2$

(c) $CH_2Cl - CHBr_2$

(d) $CHCl_2 - CHCl_2$

Ans : (b) $CH_3 - CHCl_2$

Geminal dihalides contain two halogen atoms attached to the same carbon atom. In $CH_3 - CHCl_2$, both chlorine atoms are bonded to the second carbon atom. Such compounds differ from vicinal dihalides where the two halogen atoms are attached to adjacent carbon atoms instead.

24. Which statement correctly describes the S_N1 reaction mechanism?

ISC 2008

(a) It occurs in one step only

(b) It involves backside attack only

(c) It proceeds through carbocation intermediate

(d) It always gives inversion of configuration

Ans : (c) It proceeds through carbocation intermediate

In the S_N1 mechanism, the leaving group first departs forming a carbocation intermediate. This step is slow and determines the overall reaction rate. Since the carbocation is planar, nucleophilic attack can occur from either side, often leading to racemisation rather than complete inversion of configuration.

25. Which of the following haloalkanes reacts most slowly in the S_N2 mechanism?

ISC 2003

(a) Methyl bromide

(b) Ethyl bromide

(c) Isopropyl bromide

(d) Tert-butyl bromide

47. Write the structure of 3 -bromo-2-methylprop-1-ene.

ISC 2024

Ans :

The structure of 3-bromo-2-methylprop-1-ene is

$$\mathrm{BrCH_2-\underset{\displaystyle \underset{\displaystyle \mathrm{CH_3}}{|}}{C}=CH_2}$$

48. Draw the structure of 2-bromopentane.

ISC 2019

Ans :

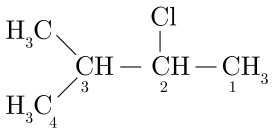
$$\mathrm{\overset{1}{C}H_3-\underset{\displaystyle \underset{\displaystyle \mathrm{Br}}{|}}{\overset{2}{C}H}-\overset{3}{C}H_2-\overset{4}{C}H_2-\overset{5}{C}H_3}$$

2-bromopentane

49. Write the IUPAC name of $(CH_3)_2CH{\cdot}CH(Cl)CH_3$

ISC 2004

Ans :



2-chloro-3-methylbutane

50. Write the chemical equation for the following reaction Acetone with sodium hypoiodite.

ISC 2005

Ans :

In the preparation of iodoform, sodium hypoiodite can also be used in place of sodium hydroxide with acetone.

$$CH_3COCH_3 + 3NaOI \longrightarrow CH_3COCl_3 + 3NaOH$$

$$CH_3COCI_3 + NaOH \longrightarrow CH_3COONa + CHI_3$$

51. What happens when ethyl chloride is treated with aqueous KOH ?

ISC 2011

Ans :

Ethyl chloride undergoes hydrolysis to form ethyl alcohol (through S_N2 nucleophilic substitution).

$$\underset{\text{Ethyl chloride}}{C_2H_5Cl} + KOH(aq) \longrightarrow \underset{\text{Ethanol}}{C_2H_5OH} + KCl$$

52. How methyl bromide be preferentially converted to methyl isocyanide?

ISC 2008

Ans :

It can be done by treating the methyl bromide with alcoholic silver cyanide.

$$CH_3Br + \underset{\text{(Alc.)}}{AgCN} \longrightarrow \underset{\substack{\text{Methyl}\\ \text{isocyanide}}}{CH_3NC} + AgBr$$

53. Write the balanced chemical equation for ethyl chloride treated with alcoholic potassium hydroxide.

ISC 2019

Ans :

When ethyl chloride is treated with alcoholic KOH, it undergoes elimination reaction to form ethene.

$$C_2H_5Cl + \text{alc. } KOH \longrightarrow C_2H_4 + KCl + H_2O$$

54. Draw the structure of the following compound 4-bromo-3 -methylpent-2-ene.

ISC 2020

Ans :

$$\mathrm{H_3\overset{1}{C}-\overset{2}{C}H=\overset{3}{\underset{\displaystyle \underset{\displaystyle \mathrm{CH_3}}{|}}{C}}-\overset{4}{\underset{\displaystyle \underset{\displaystyle \mathrm{Br}}{|}}{C}}H\overset{5}{C}H_3}$$

4-bromo-3-methylpent-2-ene

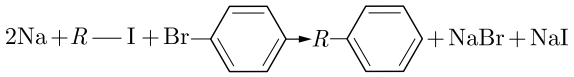
55. Give the balanced equation for the following name reaction.

ISC 2016

Wurtz-Fittig reaction

Ans :

Wurtz-Fittig reaction



56. Write the IUPAC name of the following compound $CH_2 = CHCH_2Br$.

ISC 2011

Ans :

$$\mathrm{\overset{1}{C}H_2=\overset{2}{C}H\overset{3}{C}H_2Br}$$

3-bromoprop-1-ene

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31. Which of the following compounds was the first chlorinated organic insecticide used extensively in agriculture?

ISC 2017

(a) Chloroform

(b) Carbon tetrachloride

(c) Freon-12

(d) DDT

Ans : (d) DDT

DDT or dichloro diphenyl trichloroethane was the first widely used chlorinated organic insecticide. It proved highly effective against insects and disease-carrying mosquitoes. However, DDT is non-biodegradable and accumulates in fatty tissues of animals, leading to ecological imbalance and serious environmental concerns over long-term use.

32. In the S_N2 mechanism, inversion of configuration occurs because:

ISC 2024

(a) The nucleophile attacks from the same side as leaving group

(b) Carbocation intermediate is formed

(c) Nucleophile attacks from the opposite side of leaving group

(d) Two reaction intermediates are produced

Ans : (c) Nucleophile attacks from the opposite side of leaving group

The S_N2 mechanism proceeds through a single-step backside attack of the nucleophile on the carbon atom attached to the leaving group. Since the attack occurs from the opposite side, the spatial arrangement around the chiral carbon reverses completely, producing inversion of configuration often called Walden inversion.

33. Which of the following compounds is mainly used as a solvent in paint removers and pharmaceutical industries?

ISC 2007

(a) Chloroform

(b) Dichloromethane

(c) Iodoform

(d) DDT

Ans : (b) Dichloromethane

Dichloromethane or methylene chloride is widely used as an industrial solvent because of its high volatility and excellent dissolving power. It is commonly employed in paint removers, metal cleaning and drug manufacturing processes. However, prolonged exposure can damage the central nervous system and cause serious health problems.

34. Which of the following factors mainly favours elimination reaction over substitution reaction in haloalkanes?

ISC 2021

(a) Use of aqueous KOH

(b) Use of dilute acids

(c) Use of alcoholic KOH and high temperature

(d) Presence of ultraviolet light only

Ans : (c) Use of alcoholic KOH and high temperature

Alcoholic KOH acts as a strong base and favours removal of hydrogen halide from haloalkanes, producing alkenes through elimination reaction. Higher temperature also promotes elimination because alkene formation increases entropy. Under these conditions, elimination becomes more favourable than nucleophilic substitution in many haloalkanes.

35. Which harmful effect is associated with prolonged exposure to chloroform?

ISC 2019

(a) Immediate explosion

(b) Ozone depletion only

(c) Liver and kidney damage

(d) Formation of acid rain

Ans : (c) Liver and kidney damage

Chronic exposure to chloroform can seriously damage the liver and kidneys because the compound is toxic to body tissues. Breathing chloroform vapours may also produce dizziness, fatigue and headache. Since chloroform can form poisonous phosgene gas on oxidation, careful handling and storage are necessary to minimise health hazards.

36. Silver acetate refluxed with bromine in carbon tetrachloride.

ISC 2021-22 (Sem-1)

(i) What are the products formed?

(a) Ethane, silver bromide and water

(b) Ethanoyl bromide and silver

(c) Ethanoic acid and silver bromide

(d) Bromomethane, silver bromide and carbon dioxide

NODIA

14. Which reaction is commonly used for preparation of higher symmetrical alkanes from alkyl halides? ISC 2024

(a) Fittig reaction

(b) Friedel-Crafts reaction

(c) Wurtz reaction

(d) Sandmeyer reaction

Ans : (c) Wurtz reaction

Wurtz reaction involves the reaction of alkyl halides with sodium metal in dry ether. Two alkyl groups combine together forming a higher symmetrical alkane. This reaction is widely used for carbon-carbon bond formation and for preparation of alkanes having greater number of carbon atoms than the starting alkyl halide.

15. The compound chloroform must be stored in dark coloured bottles because: ISC 2004

(a) It evaporates rapidly in sunlight

(b) It reacts with water immediately

(c) It forms explosive mixtures with oxygen

(d) It undergoes oxidation forming poisonous phosgene gas

Ans : (d) It undergoes oxidation forming poisonous phosgene gas

Chloroform slowly reacts with atmospheric oxygen in the presence of light producing carbonyl chloride or phosgene gas, which is highly poisonous. Dark coloured bottles prevent entry of light and minimise this oxidation process. Completely filled bottles further reduce contact with air and ensure safer storage conditions.

16. Benzyl chloride undergoes nucleophilic substitution reactions more rapidly than chlorobenzene because: ISC 2021

(a) Benzyl chloride contains weaker carbon-carbon bond

(b) Benzyl carbocation is resonance stabilised

(c) Chlorobenzene is insoluble in water

(d) Benzyl chloride possesses lower molecular mass

Ans : (b) Benzyl carbocation is resonance stabilised

In benzyl chloride, the intermediate benzyl carbocation formed during substitution is stabilised by resonance with the benzene ring. This stabilisation lowers the activation energy of the reaction and increases the reaction rate. Chlorobenzene, however, possesses partial double bond character in the carbon-chlorine bond, reducing its reactivity considerably.

17. Which of the following haloalkanes will undergo elimination reaction most readily? ISC 2020

(a) Chloromethane

(b) Ethyl chloride

(c) Isopropyl chloride

(d) Tert-butyl chloride

Ans : (d) Tert-butyl chloride

Elimination reactions proceed more readily in tertiary haloalkanes because the resulting alkene becomes highly substituted and stable. Tert-butyl chloride easily undergoes dehydrohalogenation with alcoholic KOH to form 2-methylpropene. The stability of the transition state and the alkene product increases the ease and rate of elimination reaction.

18. Which of the following compounds is expected to show optical isomerism? ISC 2014

(a) 2-Bromobutane

(b) 2-Bromopropane

(c) Ethyl bromide

(d) Tert-butyl chloride

Ans : (a) 2-Bromobutane

Optical isomerism arises when a molecule contains a chiral carbon attached to four different groups. In 2-bromobutane, the carbon bonded to bromine is attached to hydrogen, bromine, methyl and ethyl groups, all different. Therefore the compound exists as two non-superimposable mirror image isomers.

19. Freons are environmentally harmful because they: ISC 2008

(a) Produce sulphur dioxide in atmosphere

(b) Increase concentration of nitrogen oxides

(c) Deplete ozone layer through radical chain reactions

(d) Cause acid rain directly

Ans : (c) Deplete ozone layer through radical chain reactions

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nitration of chlorobenzene) leads to the formation of *m*-nitrochlorobenzene because —NO_2, group deactivates the ring because it is meta-directing.

41. **Assertion (A)** Haloalkanes when treated with alcoholic KCN forms alkane nitrile as a major product.

Reason (R) Potassium cyanide is a covalent compound.

ISC Specimen 2021-22 (Sem-I)

(a) Both (A) and (R) are correct and (R) is the correct explanation for (A).

(b) Both (A) and (R) are correct but (R) is not the correct explanation for (A).

(c) (A) is correct but (R) is incorrect.

(d) (A) is incorrect but (R) is correct.

Ans : (b) Both (A) and (R) are correct but (R) is not the correct explanation for (A).

Correct reason is potassium cyanide is an ionic compound and provides cyanide ions in solution.

42. **Assertion (A)** Addition of bromine water to 1-butene gives two optical isomers.

ISC 2023

Reason (R) The product formed contains two asymmetric carbon atoms.

(a) Both (A) and (R) are correct and (R) is the correct explanation of (A).

(b) Both (A) and (R) are correct but (R) is not the correct explanation of (A).

(c) (A) is correct and (R) is incorrect.

(d) (A) is incorrect and (R) is correct.

Ans : (c) (A) is correct and (R) is incorrect.

The reaction is

$$\underset{\text{1-butene}}{CH_2=CH-CH_2-CH_3} \xrightarrow{Br_2,\ \text{water}} \underset{\quad\quad\quad\quad\quad\quad}{\overset{Br\quad\ Br}{|\quad\ \ |}\ CH_2-\underset{*}{CH}-CH_2-CH_3}$$

The product formed contains only 1 asymmetric carbon. Hence, number of optical isomers = 2

FILL IN THE BLANK

43. A _____ precipitate is obtained on adding iodine and sodium hydroxide to _____

ISC 2012, 2008, 2006

Ans :

When acetone is heated with iodine and sodium hydroxide, a yellow precipitate of iodoform is formed.

$$\underset{\text{Acetone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3} + 3I_2 + 4NaOH \xrightarrow{\text{Heat}}$$

$$\underset{\substack{\text{Indoform}\\(\text{Yellow ppt.})}}{CHI_3} + 3NaI + CH_3-\overset{\overset{O}{\|}}{C}-\overset{-\ +}{ONa} + 3H_2O$$

ONE MARK QUESTIONS

44. Correct the following statement.

When acetone is treated with bleaching powder, chloroform is obtained.

ISC 2007

Ans :

When acetone is treated with bleaching powder, chloroform is obtained.

45. Out of ethyl bromide and ethyl chloride, which has higher boiling point and why?

ISC 2015

Ans :

For the same alkyl group, boiling point increases with the size of the halogen atom. Thus, boiling point of ethyl bromide is higher than ethyl chloride.

46. Write the structure of 1-bromo-4-chlorobut-2-ene.

ISC 2012

Ans :

The structure of 1-bromo-4-chlorobut-2-ene is

$$\overset{\quad\quad\quad\quad\quad\quad}{\overset{Cl}{|}\quad\quad\quad\quad\quad\quad\ \ \overset{Br}{|}}\ H_2C-CH=CH-CH_2$$

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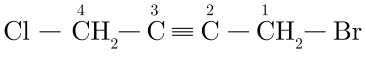
65. Write the IUPAC name of $ClCH_2C \equiv CCH_2Br$.

ISC 2024

Ans :

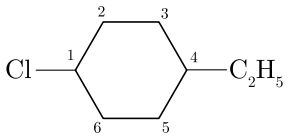


1-bromo-4-chlorobut-2-yne

66. Draw the structure of the compound, 1-chloro-4-ethylcyclohexane.

ISC 2010

Ans :

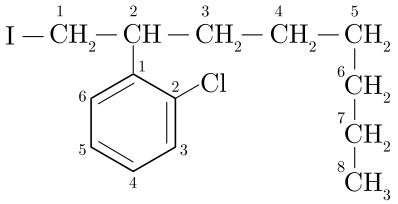


1-chloro-4-ethylcyclohexane

67. Draw the structure of 2-(2-chlorophenyl)-1-iodooctane.

ISC 2022

Ans :

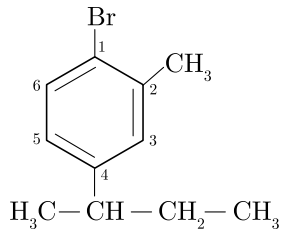


2-(2-chlorophenyl)-1-iodooctane

68. Draw the structure of the following compound: 1-bromo-4-sec-buty1-2-methylbenzene

ISC 2021

Ans :



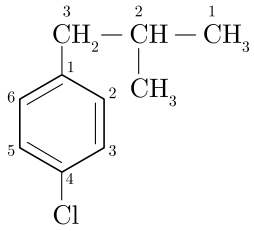
1-bromo-4-sec-butyl-2-methylbenzene

NODIA

69. Draw the structure of the following compound: 3-(4-chlorophenyl)-2-methylpropane

ISC 2004

Ans :

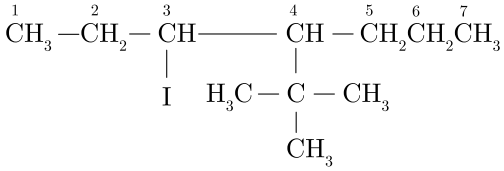


3-(4-chlorophenyl)-2-methylpropane

70. Draw the structure of the compound, 4-tent-butyl-3-iodoheptane.

ISC 2001

Ans :

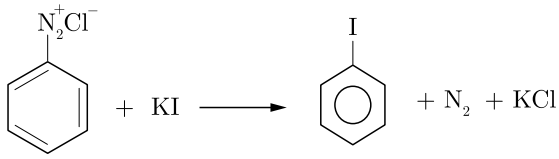


4-tert-butyl-3-iodoheptane

71. Write a chemical reaction in which the iodide ion replaces the diazonium group in a diazonium salt.

ISC 2014

Ans :



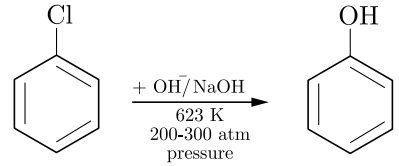
Benzene diazonium chloride (Diazonium salt)

Iodobenzene

72. How can the following conversions be brought about ? Chlorobenzene to phenol

ISC 2015

Ans :



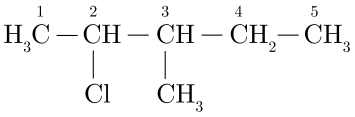
Chlorobenzene

Phenol

57. Draw the structure of the following organic compound: 2-chloro-3-methylpentane.

ISC 2018

Ans :

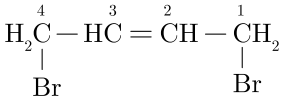


2-chloro-3-methylpentane

58. Draw the structure of 1, 4-dibromobut-2-ene.

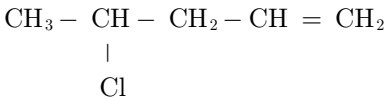
ISC 2019

Ans :



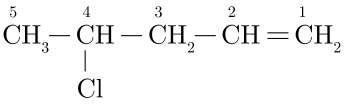
1, 4-dibromobut-2-ene

59. Write the IUPAC name of



ISC 2017

Ans :

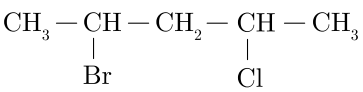


4-chloropent-1-ene

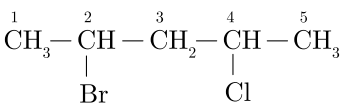
(As double bond is given preference over halogen)

60. Write the IUPAC name of the following compound.

ISC 2013



Ans :



2-bromo-4-chloropentane

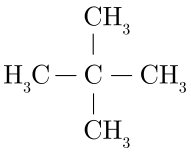
Numbering will be done in alphabetically manner.

61. A hydrocarbon C_5H_{12} gives only one monochlorination product. Identify the hydrocarbon.

ISC 2018

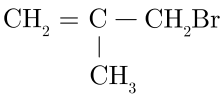
Ans :

Hydrocarbon which gives only one monochlorination product is

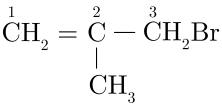


62. Give the IUPAC name of the following compound.

ISC 2022



Ans :

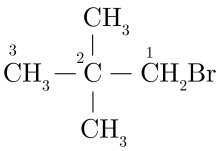


3-bromo-2-methylprop-1-ene

63. Write the IUPAC name of the following compound $(CH_3)_3CCH_2Br$.

ISC 2023

Ans :

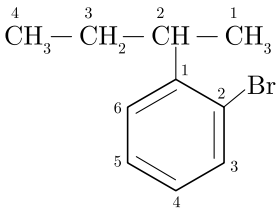


1-bromo-2, 2-dimenthylpropane

64. Draw the structure of 2-(2-bromophenyl) butane.

ISC 2020

Ans :



2-(2-bromophenyl) butane

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Ans : (d) Tert-butyl bromide

S_N2 reactions require direct backside attack by the nucleophile. In tert-butyl bromide, three bulky alkyl groups surround the carbon atom attached to bromine, creating severe steric hindrance. This prevents effective nucleophilic attack and therefore tert-butyl bromide reacts extremely slowly through the S_N2 mechanism.

26. In Wurtz-Fittig reaction, a mixture of alkyl halide and aryl halide reacts with sodium metal in dry ether to form:

ISC 2009

(a) Alkene

(b) Ketone

(c) Alkyl arene

(d) Alcohol

Ans : (c) Alkyl arene

Wurtz-Fittig reaction involves coupling between an alkyl halide and an aryl halide in the presence of sodium metal and dry ether. The reaction results in formation of alkyl-substituted aromatic compounds. This reaction is important for carbon-carbon bond formation between aliphatic and aromatic carbon atoms in organic synthesis.

27. Which of the following compounds is most likely to undergo the S_N1 mechanism rapidly?

ISC 2016

(a) Methyl chloride

(b) Ethyl chloride

(c) Isopropyl chloride

(d) Tert-butyl chloride

Ans : (d) Tert-butyl chloride

S_N1 reactions proceed through formation of a carbocation intermediate. Tertiary carbocations are highly stable because of inductive effect and hyperconjugation from surrounding alkyl groups. Therefore tert-butyl chloride undergoes ionisation most readily and reacts rapidly through the S_N1 mechanism compared with primary or secondary haloalkanes.

28. The compound $CH_2 = CHCl$ is commonly known as:

ISC 2020

(a) Allyl chloride

(b) Benzyl chloride

(c) Vinyl chloride

(d) Ethyl chloride

Ans : (c) Vinyl chloride

Vinyl chloride is the common name of chloroethene, represented by the formula $CH_2 = CHCl$. In this compound, chlorine is directly attached to an sp^2 hybridised carbon atom of the double bond. Vinyl chloride is industrially important because it is used for manufacturing polyvinyl chloride (PVC).

29. Which statement correctly explains why a racemic mixture is optically inactive?

ISC 2005

(a) It contains only one enantiomer

(b) Both enantiomers rotate light in the same direction

(c) Equal and opposite optical rotations cancel each other

(d) Racemic mixtures do not contain chiral molecules

Ans : (c) Equal and opposite optical rotations cancel each other

A racemic mixture contains equal amounts of dextrorotatory and levorotatory enantiomers. One enantiomer rotates plane polarised light clockwise while the other rotates it anticlockwise by the same magnitude. These opposite rotations cancel each other completely, making the overall mixture optically inactive despite containing chiral molecules.

30. Which reagent is commonly used to distinguish between haloalkanes and haloarenes through hydrolysis reactions?

ISC 2025

(a) Aqueous KOH

(b) Concentrated H_2SO_4

(c) Sodium bicarbonate

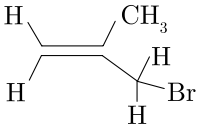
(d) Bromine water

Ans : (a) Aqueous KOH

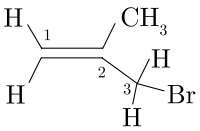
Haloalkanes readily undergo hydrolysis with aqueous KOH producing alcohols because the carbon-halogen bond breaks relatively easily. Haloarenes resist hydrolysis due to resonance stabilisation and partial double bond character in the carbon-halogen bond. Therefore aqueous KOH helps distinguish haloalkanes from haloarenes based on their reactivity.

NODIA

73. Write the IUPAC name of the following compound.
ISC 2001

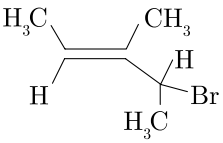


Ans :

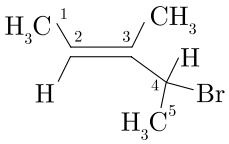


3-bromo-2-methylprop-1-ene

74. Give the IUPAC name of the following compound.
ISC 2003

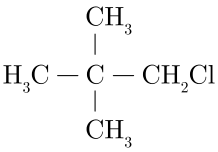


Ans :

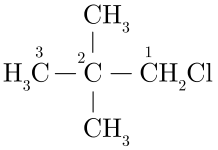


4-bromo-3-methylpent-2-ene

75. Write the IUPAC name of the following compound:
ISC 2008



Ans :



1-chloro-2,2-dimethylpropane

76. Complete the following chemical equation, Peroxide
ISC 2023

$$CH_3CH_2CH = CH_2 + HBr \xrightarrow{\text{Peroxide}}$$

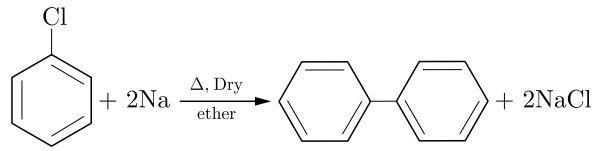
Ans :

$$CH_3CH_2CH = CH_2 + HBr \xrightarrow{\text{Peroxide}} \underset{1-\text{bromobutane(Major)}}{CH_3 - CH_2 - CH_2 - CH_2Br} + \underset{\text{(Minor)}}{CH_3 - CH_2 - CH(Br)CH_3}$$

77. What will be the product formed when chlorobenzene is heated with sodium metal in the presence of dry ether?
ISC 2015

Ans :

Chlorobenzene is heated with sodium metal in the presence of dry ether gives diphenyl compound.

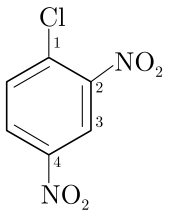


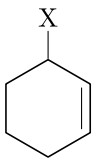
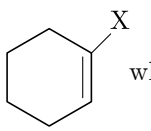
Chlorobenzene Diphenyl compound

78. Write the structure of 2, 4-dinitrochlorobenzene.
ISC 2017

Ans :

The structure of 2, 4-dinitrochlorobenzene is



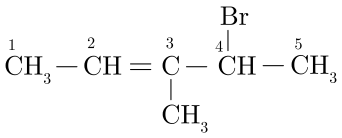
79. Out of  and  which one is an example of allylic halide?
ISC 2025

Ans :

In allylic halides, the halogen is bonded to the sp^3 -hybridised carbon atom next to a carbon-carbon double bond.

Downloaded from www.pdf.tube

(ii)



4-bromo-3-methylpent-2-ene

125. Write chemical equations when

ISC 2024

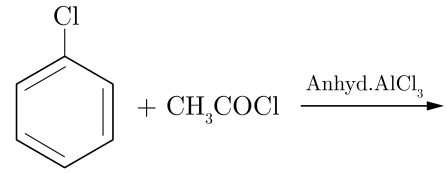
(i) ethyl chloride is treated with aqueous KOH.

(ii) chlorobenzene is treated with CH_3COCl in the presence of anhydrous $AlCl_3$.

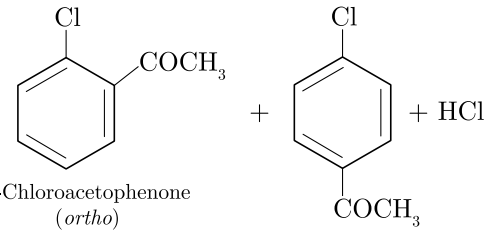
Ans :

(i) $\underset{\text{Ethyl chloride}}{CH_3-CH_2-Cl} + KOH(aq) \longrightarrow \underset{\text{Ethanol}}{CH_3CH_2OH} + KCl$

(ii)



Chlorobenzene



2-Chloroacetophenone (*ortho*)

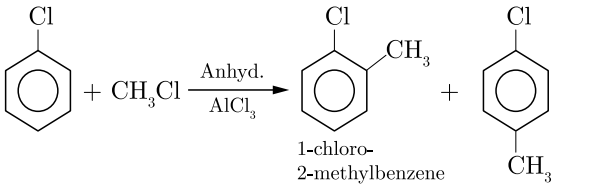
4-Chloroacetophenone (*para*)

126. Explain the following reactions with an example: Friedel-Crafts reaction.

ISC 2010

Ans :

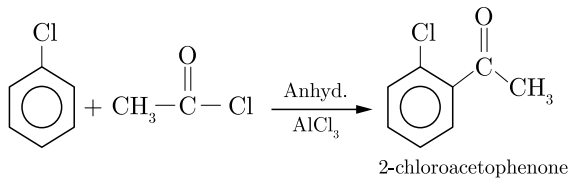
Haloarenes in presence of Lewis acid react with alkyl halide or acid halide to give a mixture of *o*- and *p*-haloalkylbenzene (or haloacylbenzene)



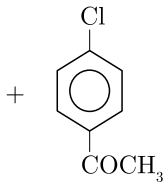
1-chloro-2-methylbenzene

1-chloro-4-methylbenzene

NODIA



2-chloroacetophenone



4-chloroacetophenone

127. Racemisation occurs in S_N1 reactions. Why?

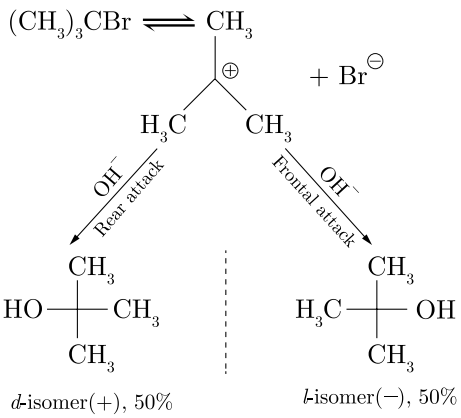
ISC 2017

Ans :

In S_N1 reaction, there is a formation of carbocation as an intermediate in rate determining step. Since, carbocation is sp^2-hybridised and planar reactive intermediate, the nucleophile can attack from both sides (above and below) of carbocation with almost equal ease.

This gives rise to 50% product with *d*-isomer (+) and 50% product with *l*-isomer (–).

Hence, product formed is racemic mixture of equal proportions of two optically active enantiomers (±).



d-isomer(+), 50%

l-isomer(−), 50%

Racemic mixture

128. Chlorobenzene is extremely less reactive towards a nucleophilic substitution reaction. Give two reasons for the same.

ISC 2002

Ans :

Two reasons for the less reactivity of chlorobenzene towards a nucleophilic substitution reaction are as follows

86. What happens when CH_3-Br is treated with KCN ?

ISC 2025

Ans :

When CH_3-Br is treated with KCN, methyl cyanide is obtained.

$$\underset{\text{Methyl bromide}}{CH_3-Br} + \underset{\text{Potassim cyanide}}{K^+-CN^-} \longrightarrow \underset{\text{Methyl cyanide}}{CH_3-CN} + \underset{\text{Potassiun bromide}}{KBr}$$

It is a nucleophilic substitution reaction. Nucleophile CN^- substitutes Br^-.

87. Predict the order of reactivity of four isomeric bromobutanes in S_N1 reaction.

ISC 2002

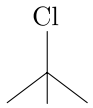
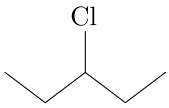
Ans :

Order of reactivity of four isomeric bromobutanes in S_N1 reaction is

$$(CH_3)_3CBr > CH_3CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_3 > (CH_3)_2CHCH_2Br > CH_3CH_2CH_2CH_2Br$$

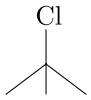
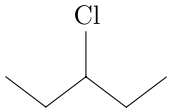
88. Which compound in the following pair undergoes faster towards S_N1 reaction?

ISC 2010

(I)  (II) 

Ans :

The reactivity towards S_N1 reaction depends upon the stability of the intermediate carbocation which an alkyl halide gives on ionisation.

As 3° carbocations are more stable than 2° carbocations, therefore,  will react faster than  in S_N1 reaction.

89. Which will react faster towards S_N2 displacement, 1-bromopentane or 2-bromopentane and why?

ISC 2017

Ans :

1-bromopentane is a primary alkyl halide while 2-bromopentane is a secondary alkyl halide. Since, primary alkyl halides are sterically less hindered therefore, 1-bromopentane reacts faster towards S_N2 reaction as in

S_N1 reactions, reactivity depends upon the stability of carbocation.

90. A solution of KOH hydrolyses $CH_3CHClCH_2CH_3$ and $CH_3CH_2CH_2CH_2Cl$. Which one of these is more easily hydrolysed?

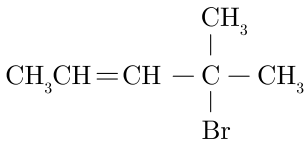
ISC 2020

Ans :

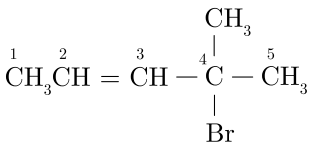
The reaction of alkyl halide with aqueous KOH occurs by S_N1 mechanism. Further, the reactivity in S_N1 depends upon the stability of carbocation. Since, $CH_3CHClCH_2CH_3$ forms more stable 2° carbocation on ionisation than $CH_3CH_2CH_2CH_2Cl$. therefore, $CH_3CHClCH_2CH_3$ hydrolyses faster than $CH_3CH_2CH_2CH_2Cl$.

91. Write the IUPAC name of

ISC 2024



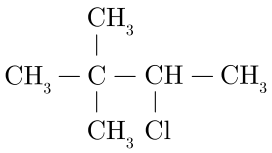
Ans :



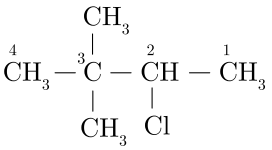
4-bromo-4-methylpent-2-ene

92. Write the IUPAC name of the following compound.

ISC 2021



Ans :



2-chloro-3, 3-dimenthylbutane

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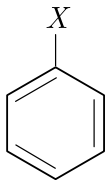


3-halocyclohex-1-ene

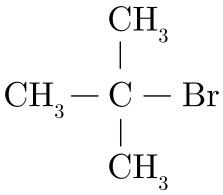
Thus, is an allylic halide.

80. Write the structure of an isomer of compound C_4H_9Br which is most reactive towards S_N1 reaction.

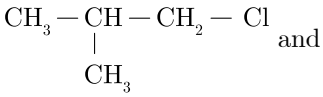
ISC 2020

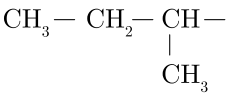
Ans :

Tertiary (3°) alkyl halides are most reactive towards S N 1 reaction followed by secondary (2°) and primary (1°) alkyl halides. C_4H_9Br has four isomer among them. The isomer,



(2-bromo -2-methylpropane) of compound C_4H_9Br is most reactive towards S_N1 reaction.

81. Out of  and

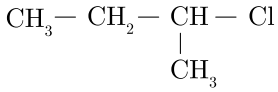


which is more reactive towards S_N1 reaction and why?

ISC 2013

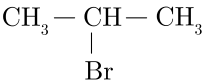
Ans :

Among the given haloalkanes,

 will undergo S_N1 reaction faster because it is a secondary alkyl halide and forms a secondary carbocation that can stabilise itself more than primary carbocation.

82. Which would undergo S_N1 reaction faster in the following pair?

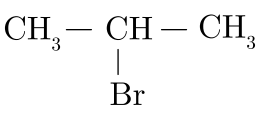
ISC 2023

$CH_3-CH_2-CH_2-Br$ and 

Ans :

Secondary alkyl halides prefer to undergo S_N1 reaction than primary alkyl halides because of formation of more stable 2° carbocation.

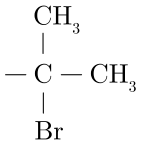
Hence, out of the given pair



would undergo S_N1 reaction faster.

83. Which would undergo S_N2 reaction faster in the following pair and why?

ISC 2024

CH_3-CH_2-Br and 

Ans :

On steric grounds, 1° alkyl halides are more reactive than tent-alkyl halides toward S_N2 reactions. Thus, CH_3-CH_2-Br would undergo S_N2 reaction faster than $[(CH_3)_3CBr]$ because it is a primary halide, i.e. less hindered.

84. Which would undergo S_N2 reaction faster in the following pair and why?

ISC 2019

CH_3-CH_2-Br and CH_3-CH_2-I

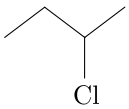
Ans :

As I^- ion is a better leaving group than Br^- ion, therefore iodides are more reactive than bromides.

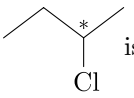
Therefore, CH_3-CH_2-I is more reactive than CH_3-CH_2-Br towards S_N2 reaction and hence, CH_3-CH_2-I would undergo S_N2 reaction faster than CH_3-CH_2-Br.

85. Identify the chiral molecule in the following pair :

ISC 2017

 and

Ans :

 is chiral molecule as it contains an asymmetric carbon atom (which is denoted by *).

TWO MARKS QUESTIONS

98. Out of S_N1 and S_N2 which reaction occurs with
ISC 2022

(a) inversion of configuration?

(b) racemisation?

Ans :

(a) S_N2 reaction occurs with inversion of configuration.

(b) S_N1 reaction proceeds with racemisation.

99. Write a chemical test to distinguish between
ISC 2025

(a) chlorobenzene and benzyl chloride

(b) chloroform and carbon tetrachloride

Ans :

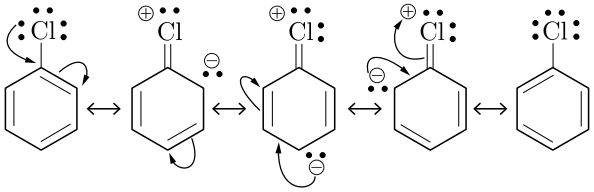
(a) Benzyl chloride when treated with $AgNO_3$ solution, will give a white ppt. while chlorobenzene will not.

(b) Chloroform when treated with 1° amine and KOH, gives offensive smelling isocyanides while CCl_4 does not give this test.

100. Draw the resonating structures of chlorobenzene.
ISC 2008

Ans :

Chlorobenzene can be represented as a resonance hybrid of the following five canonical forms.

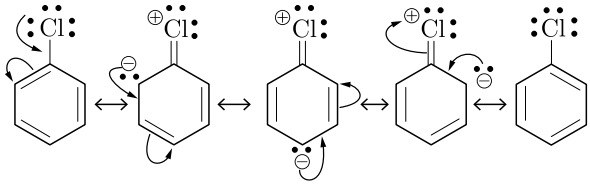


From the above canonical forms, it is clear that C – Cl bond in chlorobenzene acquires a partial double bond character. This shortens C – Cl bond length and imparts stability to the molecule.

101. Why is methyl chloride hydrolysed more easily than chlorobenzene?
ISC 2021

Ans :

Chlorobenzene is stabilised by resonance so, has a double bond character between C and Cl. Secondly, C is sp^2-hybridised so, more electronegative, thus Cl^- is not replaced easily.



While in methyl chloride, C – Cl has a single bond character which can be cleaved easily and hence, it is hydrolysed more easily than chlorobenzene.

102. What will be the major product obtained when 2-bromobutane reacts with alcoholic potassium hydroxide? State the type of reaction involved in it.
ISC Specimen 2018

Ans :

$$CH_3-CH_2-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_3 \ + \underset{\text{(Alc.)}}{KOH} \longrightarrow$$

$$\underset{\text{But-1-ene (Minor)}}{CH_3CH_2-CH=CH_2} + \underset{\text{But-2-ene (Major)}}{CH_3-CH=CHCH_3}$$

The type of reaction involved in above case is β -elimination.

103. Complete the following reactions.
ISC 2013

(i) $C_6H_5N_2Cl + KI \longrightarrow$

(ii) $\begin{matrix} H & & H \\ & C=C & \\ H & & H \end{matrix} + Br_2 \xrightarrow{CCl_4}$

Ans :

(i) $C_6H_5N_2^+Cl^- + KI \longrightarrow \underset{\text{Iodobenzene}}{C_6H_5I} + KCl + N_2\uparrow$

(ii) $\begin{matrix} H & & H \\ & C=C & \\ H & & H \end{matrix} + Br_2 \xrightarrow{CCl_4} Br-CH_2-CH_2-Br$

1, 2-dibromoethane

104. How will you convert the following?
ISC 2020

(i) Chlorobenzene to biphenyl

(ii) Propene to 1-bromopropane

Ans :

(i) Chlorobenzene to biphenyl Refer to text on page 117 (Fittig reaction).

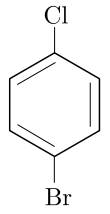
NODIA

93. Draw the structures of the following organic halogen compounds. ISC 2000

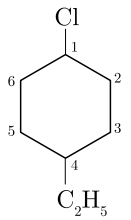
(i) *p*-bromochlorobenzene

(ii) 1-chloro-4-ethylcyclohexane

Ans :

(i) 

p-bromochlorobenzene

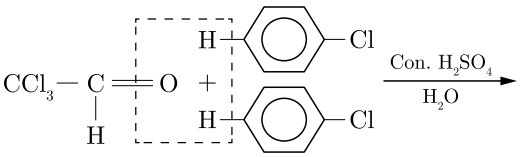
(ii) 

1-chloro-4-ethylcyclohexane

94. Write the balanced equation for the preparation of DDT. ISC 2008

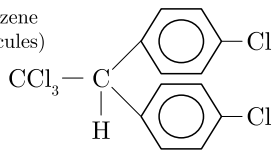
Ans :

DDT is prepared by heating chlorobenzene with chloral in the presence of concentrated sulphuric acid.



Trichloroethanal (Chloral)

Chlorobenzene (Two molecules)



95. Give the balanced equation for the following reaction. 1-butanol and hydrogen chloride (in presence of $ZnCl_2$). ISC 2012

Ans :

$ZnCl_2$ is dehydrating agent, i.e. remove water molecule.

When alcohols are treated with halogen acid in the presence of dehydrating agent $ZnCl_2$ — OH group is replaced by halogen followed by dehydration.

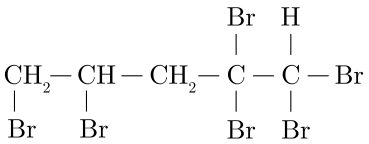
$$\underset{\text{Butanol}}{CH_3CH_2CH_2CH_2-OH} + \underset{\substack{\text{Hydrogen}\\\text{chloride}}}{HCl} \xrightarrow{ZnCl_2} \underset{\text{Chlorobutane}}{Cl-CH_2CH_2CH_2CH_3} + H_2O$$

96. What happens when bromine attacks ISC 2019

$$CH_2=CH-CH_2-C\equiv CH\ ?$$

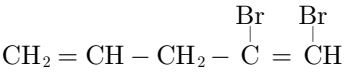
Ans :

$$CH_2=CH-CH_2-C\equiv CH \xrightarrow{Br_2}$$

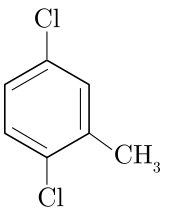


This product is formed when Br_2 is used in excess. But if only one mole of Br_2 is used, the following product will be formed.

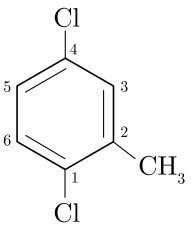
$$CH_2=CH-CH_2-C\equiv CH \xrightarrow[(1\text{ mol})]{Br_2}$$



97. Write the IUPAC name of the following compound: ISC 2014



Ans :



1, 4-dichloro-2-methylbenzene

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110. Write the mechanism of the following reaction.

ISC 2023

$$CH_3CH_2OH \xrightarrow{HBr} CH_3CH_2Br + H_2O$$

Ans :

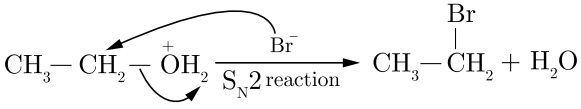
The mechanism of the given reaction is as follows

Step I $HBr \longrightarrow H^+ + Br^-$

Step II Protonation of alcohol

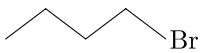
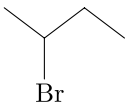
$$CH_3 - CH_2 - OH + H^+ \longrightarrow \underset{\text{Protonated alcohol}}{CH_3 - CH_2 - \overset{+}{O}H_2}$$

Step III Nucleophilic attack of Br^-

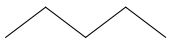


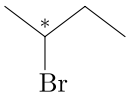
111. Which alkyl halide from the following pair is chiral and which one can undergoes faster towards S_N2 reactions?

ISC 2017

(a)  (b) 

Ans :

(a)  Br undergoes faster towards S_N2 reaction as it is a primary halide.

(b) The alkyl halide  is chiral as it contains asymmetric carbon (*) atom.

112. Which compound in each of the following pairs will react faster towards S_N2 reaction with — OH?

ISC 2025

Why?

(i) CH_3Br or CH_3I

(ii) $(CH_3)_3CCl$ or CH_3Cl

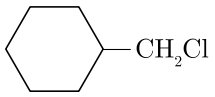
Ans :

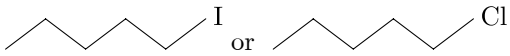
(i) CH_3I will react faster as compared to CH_3Br because CH_3I has lower bond dissociation energy and I^- is a better leaving group than Br^-. Thus, in the presence of nucleophile, iodide ion will be released at a faster rate.

(ii) CH_3Cl being a 1° halide will react faster as compared to $(CH_3)_3CCl$ which is a 3° halide because 1° halides undergo S_N2 mechanism faster than 3° halides.

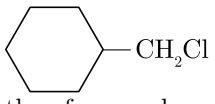
113. Which one in the following pairs of substances undergoes S_N2 substitution reaction faster and why?

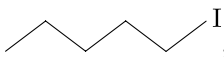
ISC 2005

(i) 

(ii) 

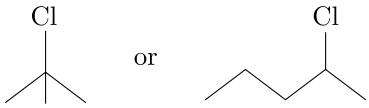
Ans :

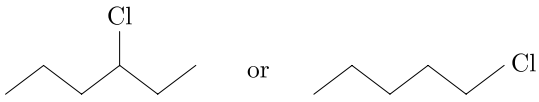
(i)  it is a primary halide and therefore, undergoes, S_N2 reaction faster.

(ii)  , as iodide ion is a better leaving group because of its larger size therefore, it undergoes S_N2 reaction faster.

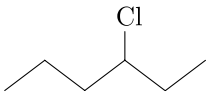
114. Which one in the following pairs undergoes S_N1 substitution reaction faster and why?

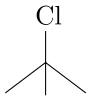
ISC 2017

(i) 

(ii) 

Ans :

(i)  tertiary halide reacts faster than secondary halide towards S_N1 reactions because of the greater stability of tertiary carbocation intermediate.

(ii)  reacts faster because of greater stability of secondary carbocation than primary.

115. Suggest a possible reason for the following observations.

ISC 2022

(i) The order of reactivity of haloalkanes is $RI > RBr > RCl$

(ii) Neo-pentyl chloride, $(CH_3)_3C - CH_2Cl$ does not follow S_N2 mechanism.

NODIA

Ans :

(i) When alkyl group is same, the reactivity of alkyl halide is decided by the halogen present. Greater the size of halogen atom, larger is the $R-X$ bond length, and weaker is the bond. Thus, more reactive is the alkyl halide. The order of size of halogen is

$$F < Cl < Br < I$$

Thus, the order of reactivity is

$$R-I > R-Br > R-Cl$$

(ii) Since, reactivity of S_N2 reactions depends upon steric hindrance and less sterically hindered molecules reacts faster in S_N2 reaction. As there is large steric hindrance in the case of neo-pentyl chloride so, it does not follow S_N2 mechanism.

116. Discuss the mechanism of S_N1 reaction of haloalkanes.

ISC 2010

Ans :

S_N1 reactions are generally carried out in polar protic solvents (like water, alcohol, acetic acid, etc). The reaction between tert-butyl bromide and hydroxide ion yields tent-butyl alcohol and follows the first order kinetics.

$$(CH_3)_3CBr + OH^- \longrightarrow (CH_3)_3COH + Br^-$$

The steps involved are

(i) Formation of carbocation intermediate

$$(CH_3)_3C-Br \xrightarrow{\text{Slow}} \underset{\text{(Carbocation)}}{(CH_3)_3C^+} + Br^-$$

(ii) Attack of nucleophile on carbocation formed leading to formation of substituted product.

$$(CH_3)_3C^+ + \underset{\text{(Nucleophile)}}{OH^-} \xrightarrow{\text{Fast}} (CH_3)_3COH$$

117. Why is it that haloalkanes are more reactive than haloarenes toward nucleophiles?

ISC 2007

Ans :

It is due to the following reasons.

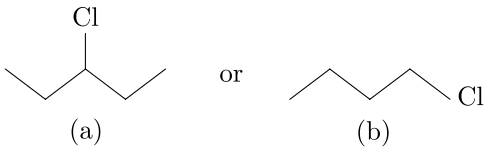
(a) In haloalkanes, there is single bond between $R-X$, which needs less bond dissociation energy to break hence, they are more reactive towards nucleophiles. In haloarenes, there is partial double bond character between $C-X$ bond due to resonance, therefore $C-X$ bond in haloarenes are more stronger and requires more bond dissociation energy to break.

(b) Carbon attached to halogen is sp^3-hybridised in haloalkanes and sp^2-hybridised in haloarenes. sp^3-hybridised carbon is less electronegative than sp^2-hybridised carbon due to less s-character. Thus, $C-X$ bond in haloalkane releases more electrons to halogen.

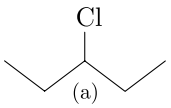
(c) It is difficult for electron rich nucleophiles to approach electron rich benzene ring in haloarenes due to repulsion while there is no such thing in haloalkanes.

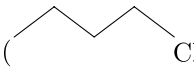
118. Which one of the following react faster towards S_N1 reaction and why?

ISC 2022



Ans :

(ii) 

will react faster towards S_N1 reaction because (a) will form more stable 2° carbocation as compared to (b) 

which forms 1° carbocation.

119. Account for the following.

ISC 2021

(i) The C — Cl bond length in chlorobenzene is shorter than that in CH_3 — Cl.

(ii) Chloroform is stored in closed dark brown bottles.

Ans :

(i) Due to partial double bond character of $C-Cl$ bond (due to resonance in C_6H_5Cl), bond length of $C-Cl$ (in chlorobenzene) is shorter than that in methyl chloride (CH_3Cl).

(ii) In the presence of air and sunlight, chloroform gets oxidised to phosgene (carbonyl chloride, $COCl_2$), a poisonous compound.
Thus, to prevent the formation of phosgene, chloroform is stored in dark brown bottles filled upto brim.

$$\underset{\text{Chloroform}}{CHCl_3} + \frac{1}{2}O_2 \xrightarrow{h\nu} \underset{\substack{\text{Carbonyl chloride}\\ \text{(Phosgene)}}}{COCl_2} + HCl$$

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120. Suggest a possible mechanism for the following reaction

$$n-\text{BuBr} + \text{KCN} \xrightarrow{\text{EtOH, H}_2\text{O}} n-\text{BuCN}$$

ISC 2009, 2008

Ans :

KCN is a reagent that gives CN^- ion as nucleophile in aqueous medium.

Resonating forms of KCN

$$K^+[:\bar{C}\equiv N:] \longleftrightarrow K^+[:C=\ddot{N}:^-]$$

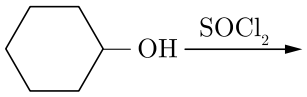
$$K^+CN^- + CH_3CH_2CH_2\overset{\delta+}{C}H_2\overset{\delta-}{Br} \longrightarrow CH_3CH_2CH_2CH_2CN + KBr$$

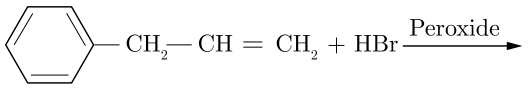
or n - BuBr + KCN $\xrightarrow{C_2H_5OH,\ H_2O}$ n - BuCN + KBr

CN^- is an ambident nucleophile therefore, it can attack either through C-atom or through N-atom. Since, C – C is a stronger bond than C – N bond, therefore it attacks through C to form n-butyl cyanide.

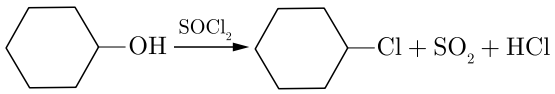
121. Draw the structure of major monohalo product in each of the following reactions.

ISC 2014

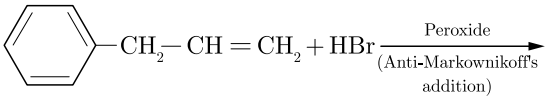
(i) 

(ii) 

Ans :

(i) 

1-chlorocyclohexane

(ii) 

122. Write the IUPAC names of the following compounds :

ISC 2013

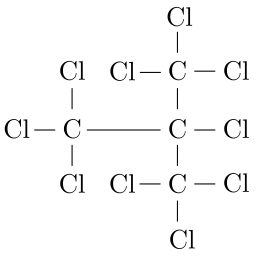
(i) $CH_2=CHCH_2Br$ (ii) $(CCl_3)_3CCl$

Ans :

(i) $\overset{1}{C}H_2=\overset{2}{C}H\overset{3}{C}H_2Br$

3-bromoprop-1-ene

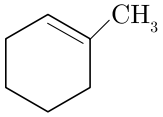
(ii) $(CCl_3)_3CCl$: The structure can be drawn as



tris-(trichloromethyl) chloromethane

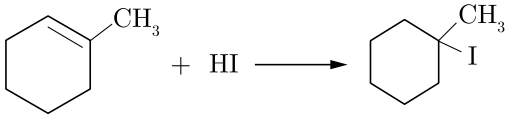
123. Complete the following reactions:

ISC 2024

(i)  + HI ⟶

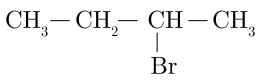
(ii) $CH_3CH_2CH=CH_2 + HBr \longrightarrow$

Ans :

(i) 

1-ioda-1-methylcyclohexane

(ii) $CH_3CH_2-CH=CH_2 + HBr \longrightarrow$



2-bromobutane

124. Draw the structures of the following organic halogen compounds:

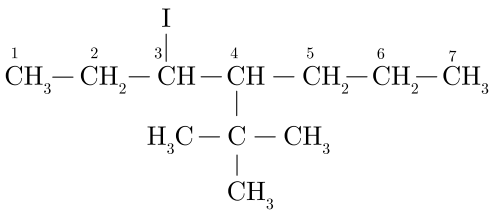
ISC 2010

(i) 4-tent-butyl-3-iodoheptane

(ii) 4-bromo-3-methylpent-2-ene

Ans :

(i)



4-tert-butyl-3-iodoheptane

NODIA

(ii) Propene to 1-bromopropane

$$\underset{\text{Propene}}{CH_3CH=CH_2} + HBr \longrightarrow \underset{\substack{\text{1-bromopropane}\\\text{(Minor)}}}{CH_3CH_2CH_2Br} + \underset{\substack{\text{2-bromopropane}\\\text{(Major)}}}{CH_3\underset{\displaystyle Br}{\underset{|}{C}}HCH_3}$$

105. Write the chemical equations when,

ISC 2010

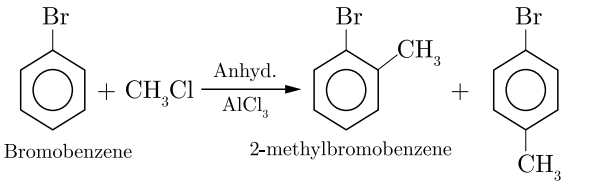
(i) methyl chloride is treated with $AgNO_2$.

(ii) bromobenzene is treated with CH_3Cl in the presence of anhydrous $AlCl_3$.

Ans :

(i) $\underset{\substack{\text{Methyl}\\\text{chloride}}}{CH_3Cl} + AgNO_2 \longrightarrow CH_3NO_2 + AgCl$

(ii)



Bromobenzene 2-methylbromobenzene 4-methylbromobenzene

106. How can the following conversion be brought about methyl chloride to acetone.

ISC 2016

Ans :

$$\underset{\substack{\text{Methyl}\\\text{chloride}}}{CH_3Cl} \xrightarrow[\text{Ether}]{Mg} \underset{\substack{\text{Methyl magnesium}\\\text{chloride}}}{CH_3MgCl}$$

$$CH_3Cl \xrightarrow{KCN} \underset{\text{Methyl cyanide}}{CH_3CN} \xrightarrow{CH_3MgCl} CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=NMgCl \xrightarrow{H_3O^+} \underset{\text{Acetone}}{CH_3-\underset{\displaystyle O}{\underset{\|}{C}}-CH_3}$$

107. Complete the following reaction and name the reaction.

$$C_3H_7NH_2 + CHCl_3 + 3KOH(alc) \xrightarrow{\Delta} ... + 3KCl + 3H_2O$$

ISC 2012, 2007

Ans :

$$C_3H_7NH_2 + CHCl_3 + 3KOH(alc.) \xrightarrow{\Delta}$$

$$\underset{\substack{\text{Propyl}\\\text{isocyanide}}}{C_3H_7N \rightleftharpoons C} + 3KCl + 3H_2O$$

(Carbylamine reaction)

When chloroform is warmed with a suitable aromatic or aliphatic primary amine and alcoholic caustic potash, corresponding isocyanide is formed which has extremely offensive smell.

108. Which alkyl halide from the following pair would you expect to react more rapidly by an S_N2 mechanism and why?

ISC 2021

$$CH_3-CH_2-\underset{\displaystyle Br}{\underset{|}{C}}H-CH_3\,;$$

$$CH_3-CH_2-CH_2-CH_2-Br$$

Ans :

In S_N2 reactions, reactivity depends upon the steric hindrance. $CH_3CH_2-CH_2-CH_2-Br$ is a primary alkyl halide while $CH_3-CH_2-\underset{\displaystyle Br}{\underset{|}{C}}H-CH_3$ is a secondary alkyl halide. Since, primary alkyl halides are sterically less hindered therefore, $CH_3CH_2CH_2CH_2Br$ reacts faster towards S_N2 reaction.

109. What are ambident nucleophiles? Give an example.

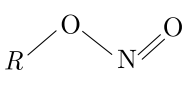
ISC 2019

Ans :

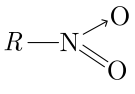
Ambident nucleophiles have two nucleophilic sites through which they can attack, e.g. nitrite ion is an ambident nucleophile. $\left[{}^{-}O-\ddot{N}=0\right]$

$$R-X+\underset{\text{Nitrite ion}}{\overline{O}-N=O} \longrightarrow \underset{\substack{\text{Alkyl}\\\text{nitrite}}}{R-O-N=O} + X^-$$

It can attack through oxygen resulting in the formation of alkyl nitrites. Also, it can attack through nitrogen resulting in the formation of nitroalkanes.



Alkyl nitrite



Nitroalkane

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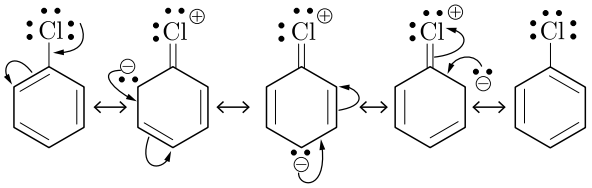
(i) **Resonance effect** The electron pair of chlorine atom is involved in conjugation with the π -electrons of the benzene ring and the following resonating structures are obtained.



As a result, electrons of $C-Cl$ bond get delocalised and a partial double bond character develops in the bond and hence, it becomes difficult for the nucleophile to cleave the $C-Cl$ bond.

(ii) **Increased electron density** A repulsion is suffered by the nucleophile due to increased electron density on the benzene ring which prohibits the nucleophile to make a close access for the attack on the molecule

129. Explain why

ISC 2008

(i) alkyl halides though polar are immiscible with water?

(ii) Grignard's reagent should be prepared under anhydrous conditions?

Ans :

(i) To be miscible with (or soluble in water) water, the solute-water force of attraction must be stronger than the solute-solute and water-water forces of attraction. Alkyl halides are polar molecules and so, held together by dipole-dipole interactions. Similarly, strong H-bonds exist between the water molecules. The new forces of attraction between the alkyl halides and water molecules is weaker than the forces of attraction already existing between alkyl halide-alkyl halide and water-water molecules. Hence, alkyl halides (though polar) are immiscible with (or insoluble in) water.

(ii) Grignard's reagents are very reactive. In the presence of moisture, they react to give alkanes.

$$\underset{\text{Grignard's reagent}}{R\overset{\delta-}{Mg}\overset{\delta+}{X}\overset{\delta-}{}} + H-OH \longrightarrow \underset{\text{Alkane}}{R-H} + Mg(OH)X$$

Therefore, Grignard's reagents should be prepared under anhydrous conditions.

THREE MARKS QUESTIONS

NODIA

130. Which compound in the following couples will react faster towards S_N2 displacement and why?

ISC 2007

(a) 1-bromopentane or 2-bromopentane

(b) 1-bromo-2-methyl butane or 2-bromo-2-methyl butane

Ans :

Reactivity of S_N2 reactions depends on steric hindrance. Therefore,

(a) 1-brompoentane will react faster because it is a primary alkyl halide and hence, less sterically hindered.

(b) 1-bromo-2-methyl butane, as it is a primary alkyl halide and less sterically hindered.

131. Given chemical equations for each of the following.

(i) Ethyl chloride is treated with aqueous KOH solution.

(ii) Chlorobenzene is treated with ammonia at 573 K and high pressure.

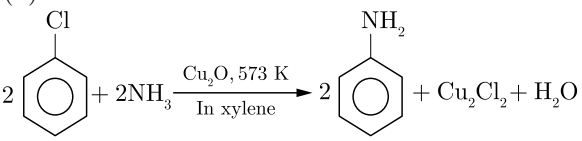
ISC 2023

Ans :

(i) Ethyl chloride undergoes hydrolysis to form ethyl alcohol (through S_N2 nucleophilic substitution)

$$\underset{\text{Ethyl chloride}}{C_2H_5Cl} + KOH(aq) \longrightarrow \underset{\text{Ethanol}}{C_2H_5OH} + KCl$$

(ii)



132. Rearrange the compounds of each of the following sets in order of reactivity towards S_N2 displacement.

ISC 2014

(i) 2-bromo-2-methylbutane,
1-bromopentane, 2-bromopentane.

(ii) 1-bromo-3-methylbutane,
2-bromo-2-methylbutane,
3-bromo-2-methylbutane.

(iii) 1-bromobutane, 1-bromo-2,2-dimethylpropane,
1-bromo-2-methylbutane,
1-bromo-3-methylbutane.

(ii) What type of hybridisation is present in the carbon atom bonded to chlorine in chlorobenzene?
(iii) Why does chlorobenzene possess a stronger carbon-chlorine bond?
(iv) Explain why chlorobenzene is less reactive towards nucleophilic substitution reactions.

Ans :
(i) Ethyl chloride.
(ii) sp^2 hybridisation.
(iii) Resonance between chlorine lone pair and benzene ring gives partial double bond character to the carbon-chlorine bond.
(iv) Due to partial double bond character, the carbon-chlorine bond becomes shorter and stronger. Therefore cleavage of the bond becomes difficult and nucleophilic substitution reactions occur very slowly.

159. A laboratory assistant noticed that bottles containing chloroform were always stored in dark coloured airtight containers completely filled with liquid. The laboratory manual warned that exposure of chloroform to air and sunlight may produce a dangerous poisonous gas. The teacher explained that oxidation of chloroform occurs slowly in the presence of oxygen and ultraviolet light. Therefore special precautions are necessary during storage and handling of chloroform in laboratories and industries.
(i) Name the poisonous gas formed during oxidation of chloroform.
(ii) Why are dark coloured bottles preferred for storage of chloroform?
(iii) Why are chloroform bottles kept completely filled?
(iv) Write the balanced chemical equation for the oxidation of chloroform.

Ans :
(i) Phosgene gas or carbonyl chloride ($COCl_2$)
(ii) Dark coloured bottles prevent exposure to light.
(iii) Completely filled bottles minimise contact of chloroform with atmospheric oxygen.
(iv) $2CHCl_3 + O_2 \rightarrow 2COCl_2 + 2HCl$

160. An environmental scientist explained the harmful effects of chlorofluorocarbons and carbon tetrachloride on the atmosphere. These compounds remain stable in the lower atmosphere and slowly diffuse into the stratosphere. Under the influence of ultraviolet radiation, they release chlorine radicals which initiate radical chain reactions destroying ozone molecules continuously. Ozone depletion allows increased penetration of harmful ultraviolet radiation to the earth's surface affecting living organisms and ecosystems.
(i) Which atmospheric layer contains the ozone layer?
(ii) Which radicals are mainly responsible for ozone depletion?
(iii) Name one chlorofluorocarbon commonly used in industries.
(iv) Mention one harmful effect of ozone depletion on human beings.

Ans :
(i) Stratosphere.
(ii) Chlorine radicals.
(iii) Freon-12 (CCl_2F_2).
(iv) Ozone depletion increases exposure to ultraviolet radiation which may cause skin cancer and eye diseases.

161. A student compared the behaviour of methyl bromide, ethyl bromide and tert-butyl bromide towards nucleophilic substitution reactions. It was observed that methyl bromide reacted fastest through the S_N2 mechanism whereas tert-butyl bromide reacted extremely slowly. The chemistry teacher explained that steric hindrance around the carbon atom attached to the halogen greatly influences the rate of bimolecular nucleophilic substitution reactions.
(i) Which haloalkane undergoes the fastest S_N2 reaction?
(ii) Which factor mainly controls the rate of S_N2 reactions?
(iii) Why does tert-butyl bromide react slowly through the S_N2 mechanism?
(iv) Why are primary haloalkanes generally more favourable for S_N2 reactions?

Ans :
(i) Methyl bromide.
(ii) Steric hindrance around the carbon atom.
(iii) In tert-butyl bromide, the carbon atom attached to bromine is surrounded by bulky alkyl groups which prevent backside attack by the nucleophile.
(iv) Primary haloalkanes possess less steric hindrance around the reactive carbon atom, therefore nucleophilic attack occurs more easily.

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- ✓ Direct copy-paste questions
- ✓ Same pattern followed

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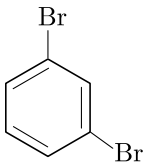
136. Give the IUPAC names of the following compounds:

ISC 2017

(i) $CH_3-\underset{\underset{Br}{|}}{CH}-CH_2-CH_3$

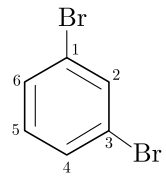
(ii) 

(iii) $CH_2=CH-CH_2-Cl$

Ans :

(i) $\overset{1}{CH_3}-\underset{\underset{Br}{|}}{\overset{2}{CH}}-\overset{3}{CH_2}-\overset{4}{CH_3}$

2-bromobutane

(ii) 

1, 3-dibromobenzene

(iii) $\overset{1}{CH_2}=\overset{2}{CH}-\overset{3}{CH_2}-Cl$

3-chloroprop-1-ene

137. How do you convert the following?

ISC 2024

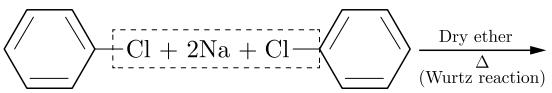
(i) Chlorobenzene to biphenyl

(ii) Propene to 1-iodopropane

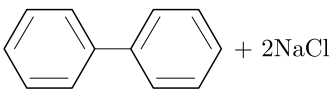
(iii) 2-bromobutane to but-2-ene

Ans :

(i) Chlorobenzene to biphenyl



Chlorobenzene Chlorobenzene



Biphenyl

(ii) Propene to 1-iodopropane

$CH_3-CH=CH_2 + HBr \xrightarrow[\text{(Anti-Markonikov's addition)}]{(C_6H_5COO)_2}$

Propene

$CH_3-CH_2CH_2Br \xrightarrow{\text{Acetone}/\Delta,\ NaI}$

1-bromopropane

$NaBr + CH_3-CH_2CH_2I$

1-iodopropane

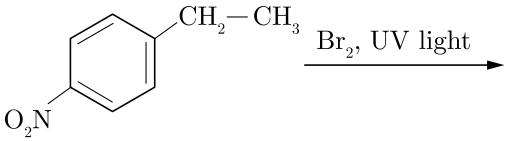
(iii) 2-bromobutane to but-2-ene

$CH_3-CH_2-\underset{\underset{Br}{|}}{CH}-CH_3 \xrightarrow[-HBr]{KOH(alc.)/\Delta} CH_3CH=CHCH_3$

2-bromobutane But-2-ene (Major product)

138. Write the major product(s) in the following.

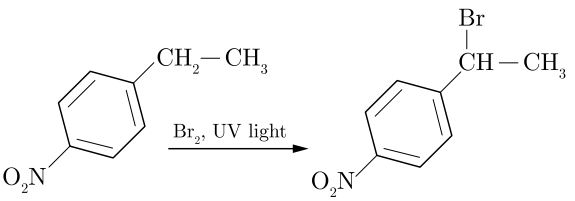
ISC 2018

(i) 

(ii) $2CH_3-\underset{\underset{Cl}{|}}{CH}-CH_3 \xrightarrow[\text{Dry ether}]{Na}$

(iii) $CH_3-CH_2-Br \xrightarrow{AgCN}$

Ans :

(i) 

4-ethyl nitrobenzene 1-(1-bromoethyl)-4-nitrobenzene

(ii) $2CH_3-\underset{\underset{Cl}{|}}{CH}-CH_3 \xrightarrow[\text{Dry ether}]{Na} CH_3-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-CH_3$

2-chloropropane 2, 3-dimenthylbutane

(iii) $CH_3-CH_2-Br \xrightarrow{AgCN}$

1-bromoethane

$CH_3-CH_2-N\rightleftharpoons C + AgBr$

Ethyl isocyanide

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FOUR MARKS QUESTIONS

144. A student treated optically active 2-bromobutane with aqueous KOH and obtained an optically inactive alcohol. Explain the reaction mechanism responsible for this observation.

ISC 2025

Ans :

The reaction proceeds through the S_N1 mechanism.

First, bromide ion leaves forming a planar carbocation intermediate.

$CH_3CHBrCH_2CH_3 \rightarrow CH_3CH^+CH_2CH_3 + Br^-\$$

The nucleophile attacks from both sides of the planar carbocation producing equal amounts of two enantiomers.

Hence racemisation occurs and the product becomes optically inactive.

145. During laboratory preparation of alkenes, a student observed that 2-bromobutane gives mainly but-2-ene on heating with alcoholic KOH. Explain this observation using Saytzeff's rule.

ISC 2018

Ans :

Alcoholic KOH causes dehydrohalogenation of 2-bromobutane.

$$CH_3CHBrCH_2CH_3 \xrightarrow{\text{alc.KOH}} CH_3CH = CHCH_3$$

According to Saytzeff's rule, the major product formed is the alkene containing the more substituted double bond.

But-2-ene is more stable because it contains a more substituted double bond than but-1-ene, therefore it forms as the major product.

146. Compare the S_N1 and S_N2 mechanisms on the basis of molecularity, stereochemistry, intermediate formation and preferred substrate.

ISC 2013

Ans :

SN1 Reaction	SN2 Reaction
Unimolecular reaction	Bimolecular reaction
Occurs in two steps	Occurs in one step
For ms carbocation intermediate	No intermediate formed
Causes racemisation	Cau ses inversion of configuration
Fav oured by tertiary haloalkanes	Fav oured by primary haloalkanes

Thus the two nucleophilic substitution mechanisms differ significantly in kinetics and stereochemistry.

147. Explain the preparation and significance of Wurtz and Wurtz-Fittig reactions in organic synthesis.

ISC 2024

Ans :

Wurtz Reaction

Alkyl halides react with sodium metal in dry ether to form higher alkanes.

$$2CH_3Br + 2Na \xrightarrow{\text{dry ether}} CH_3CH_3 + 2NaBr$$

Wurtz-Fittig Reaction

Alkyl halide and aryl halide react with sodium metal in dry ether to form alkyl benzene.

$$C_6H_5Br + CH_3Br + 2Na \xrightarrow{\text{dry ether}} C_6H_5CH_3 + 2NaBr$$

These reactions are important for carbon-carbon bond formation.

148. A student studied the optical activity of 2-bromobutane. Explain the terms asymmetric carbon, enantiomers and racemic mixture using this compound as an example.

ISC 2004

Ans :

In 2-bromobutane, the second carbon atom is attached to four different groups and is therefore called an asymmetric carbon atom.

The compound exists as two non-superimposable mirror images called enantiomers.

One enantiomer rotates plane polarised light clockwise while the other rotates it anticlockwise.

An equimolar mixture of both enantiomers is called a racemic mixture and becomes optically inactive.

149. Explain the harmful effects of freons and carbon tetrachloride on human health and environment.

ISC 2000

Ans :

Freons release chlorine radicals in the stratosphere which destroy ozone molecules through radical chain reactions.

Ozone depletion increases harmful ultraviolet radiation reaching the earth.

This may lead to skin cancer and eye disorders.

Carbon tetrachloride damages the nervous system and may affect heart functioning.

It also contributes to ozone layer depletion and environmental imbalance.

NODIA

$$H_3C-CH_2-CH=CH-CH_3 \xrightarrow{OH^-}$$

Pent-2-ene(81%)
(Major product)

$$H_3C-CH_2-CH_2-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_3$$

2-bromopentane

$$\downarrow OH^-$$

$$H_3C-CH_2-CH_2-CH=CH_2$$

Pent-1-ene
(19%)
(Minor product)

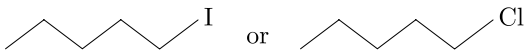
142. Answer the following questions:

ISC 2004

(i) What is meant by chirality of a compound? Give an example.

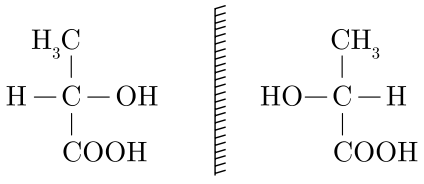
(ii) Which one of the following compounds is more easily hydrolysed by KOH and why?
$CH_3CHClCH_2CH_3$ or $CH_3CH_2CH_2CH_2Cl$

(iii) Which one undergoes S_N2 substitution reaction faster and why?



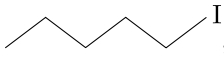
Ans :

(i) An object or molecule which is non-superimposable on its mirror image is called chiral and the property of being chiral is known as chirality. e.g. Lactic acid, $CH_3CH(OH)COOH$



(ii) $CH_3-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_2CH_3$ is more easily hydrolysed by

KOH because this hydrolysis occurs through S_N1 mechanism and this alkyl halide forms a more stable 2° carbocation than $CH_3-CH_2-CH_2-CH_2Cl$ which forms a less stable 1° carbocation.

(iii) 

, as iodide ion is a better leaving group because of its larger size therefore, it undergoes S_N2 reaction faster.

143. Following compounds are given to you.
2-bromopentane, 2-bromo-2-methylbutane, 1-bromopentane

ISC 2022

(i) Write the compound which is most reactive towards S_N2 reaction.

(ii) Write the compound which is optically active.

(iii) Write the compound which is most reactive towards β-elimination reaction.

Ans :

(i) S_N2 reactions involve the formation of transition state. Higher the steric hinderance, lesser the stability of transition state and lower is their reactivity towards S_N2.

$$\underset{\text{1-bromopentane}\ (1°)}{CH_3CH_2CH_2CH_2CH_2Br} > \underset{\text{2-bromopentane}\ (2°)}{CH_3\underset{\displaystyle Br}{\underset{|}{CH}}CH_2CH_2CH_3} > \underset{\text{2-bromo-2-methylbutane}\ (3°)}{CH_3\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle Br}{\overset{|}{C}}}}CH_2CH_3}$$

(ii) Among the given compounds, 2-bromopentane is optically active due to presence of chiral carbon (*)

$$C_3H_7-\overset{\displaystyle H}{\overset{|}{\overset{*}{C}}}-CH_3$$
$$\underset{\displaystyle Br}{|}$$

(iii) 2-bromo-2-methylbutane is the most reactive towards β-elimination reaction because in this case more substituted alkene is the major product.

$$CH_3CH_2\underset{\displaystyle Br}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CH_3 \xrightarrow[-HBr]{} \underset{\text{2-methyl but-2-ene}}{CH_3CH=\overset{\displaystyle CH_3}{\overset{|}{C}}-CH_3}$$

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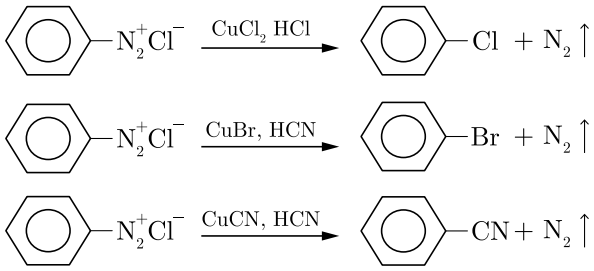
139. Write the balanced chemical equations for the following name reactions. ISC 2023

(i) Sandmeyer's reaction
(ii) Wurtz reaction
(iii) Finkelstein reaction

Ans :

(i) **Sandmeyer's reaction** In this reaction, replacement of the diazonium group by chloride, bromide and cyanide takes place. Nucleophiles such as CN^-, Cl^- and Br^- replace the diazonium group if appropriate cuprous salt is added to the solution containing diazonium group.



(ii) **Wurtz reaction** When two molecules of alkyl halides (same or different) reacts with metallic sodium in the presence of ether to form alkane.

$$R-X+R-X \xrightarrow[\text{ether}]{\text{Na, Dry}} \underset{\text{Alkane}}{R-R}$$

(iii) **Finkelstein reaction** Alkyl iodide are often prepared by the reaction of chlorides/ bromides with NaI in dry acetone.

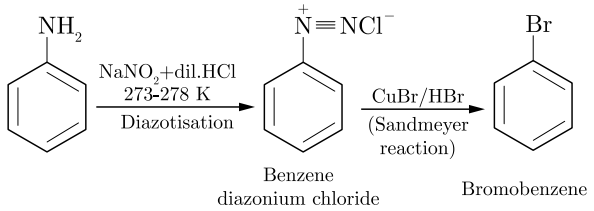
$$R-X+\text{NaI} \xrightarrow[\text{Reflux}]{\text{Acetone}} R-I+\text{Na}X$$

140. How can the following conversions be carried out? ISC 2025

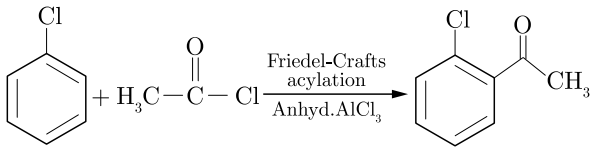
(i) Aniline to bromobenzene
(ii) Chlorobenzene to 2-chloroacetophenone
(iii) Chloroethane to butane

Ans :

(i) Aniline to bromobenzene



(ii) Chlorobenzene to 2-chloroacetophenone



(iii) Chloroethane to butane

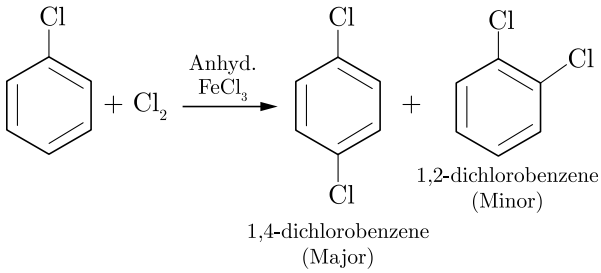
$$\underset{\text{Chloroethane}}{2CH_3CH_2Cl} + 2Na \xrightarrow[\text{Wurtz reaction (-2NaCl)}]{\text{Dry ether}} \underset{n\text{-butane}}{CH_3CH_2-CH_2-CH_3}$$

141. What happens when ISC 2019

(i) chlorobenzene is treated with $Cl_2/FeCl_3$?
(ii) ethyl chloride is treated with $AgNO_2$?
(iii) 2-bromopentane is treated with alcoholic KOH? Write the chemical equations in support of your answer.

Ans :

(i) When chlorobenzene is treated with $Cl_2/FeCl_3$, two types of products are formed as



(ii) When ethyl chloride is treated with $AgNO_2$, nitroethane is formed.

$$CH_3CH_2Cl + AgNO_2 \longrightarrow CH_3CH_2NO_2 + AgCl$$

(iii) When 2-bromopentane is treated with alcoholic KOH, it undergoes dehydrohalogenation leading to the formation of two or more different products depending upon the number of different types of β-hydrogen available.

The more highly substituted alkene (i.e. having lesser number of hydrogen atoms on the doubly bonded carbon atoms) is the major product of dehydrohalogenation. This is in accordance to Saytzeff rule.

NODIA

150. A laboratory assistant was instructed to store chloroform in airtight dark coloured bottles completely filled with liquid. Explain the reason behind this precaution.

ISC 2017

Ans :

Chloroform slowly reacts with oxygen in the presence of light.

$2CHCl_3 + O_2 \rightarrow 2COCl_2 + 2HCl$

The product carbonyl chloride or phosgene gas is highly poisonous.

Dark coloured bottles prevent exposure to light while completely filled bottles minimise contact with air.

Therefore oxidation of chloroform is prevented during storage.

151. Explain why tertiary haloalkanes undergo elimination reactions more readily than primary haloalkanes.

ISC 2002

Ans :

Tertiary haloalkanes form more stable alkenes during elimination reactions.

The transition state and intermediate species are stabilised by inductive effect and hyperconjugation.

Due to steric hindrance, nucleophilic substitution becomes less favourable.

Therefore tertiary haloalkanes preferentially undergo dehydrohalogenation with alcoholic KOH forming alkenes more readily than primary haloalkanes.

152. Distinguish between vicinal and geminal dihalides giving one example of each. Mention one method of formation for both types.

ISC 2021

Ans :

Vicinal Dihalides	**Geminal Dihalides**
Hal ogen atoms are att ached to adjacent carbon atoms	Hal ogen atoms are att ached to the same carbon atom
Exa mple: CH_2 Cl-CH_2 Cl	Example: CH_3CHCl_2
Formed by addition of halogens to alkenes	Formed by substitution reactions

Thus the two types differ in position of halogen atoms and method of preparation.

153. A chemist found that chlorobenzene does not undergo hydrolysis easily with aqueous KOH unlike ethyl chloride. Explain the reason for this difference in reactivity.

ISC 2010

Ans :

In chlorobenzene, resonance occurs between the lone pair electrons of chlorine and the benzene ring.

This gives partial double bond character to the carbon-chlorine bond.

As a result the bond becomes shorter and stronger than the corresponding bond in haloalkanes.

Additionally, the carbon attached to chlorine is sp^2 hybridised.

Therefore chlorobenzene resists nucleophilic substitution reactions.

154. Give reasons.

ISC 2023

(i) C — Cl bond length in chlorobenzene is shorter than C — Cl bond length in CH_3 — Cl.

(ii) The dipole moment of chlorobenzene is lower than that of cyclohexyl chloride.

(iii) S_N1 reactions are accompanied by racemisation in optically active alkyl halides.

Ans :

(i) In chlorobenzene, the lone pair of electrons present on Cl-atom are in conjugation with n-electrons of the benzene ring.
As a result, $C-Cl$ bond acquires some double bond character while in CH_3-Cl, bond is a pure single bond. Since, bond length of $C-Cl$ single bond is greater than $C-Cl$ partial double bond. Therefore, $C-Cl$ bond in halobenzene is shorter than that in CH_3-Cl.

(ii) Due to greater *s*-character, sp^2-hybridised carbon atom of chlorobenzene is more electronegative than a sp^3-hybridised carbon atom of cyclohexyl chloride.
Therefore, sp^2-hybridised carbon of $C-Cl$ bond in chlorobenzene has less tendency to release electrons to Cl than a sp^3-hybrid carbon of cyclohexyl chloride. As a result, $C-Cl$ bond in chlorobenzene is less polar than in cyclohexyl chloride.
[In other words, the magnitude of negative charge is less on Cl-atom of chlorobenzene than in cyclohexyl chloride. Further, due to

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Ans :

(i) 1-bromopentane > 2-bromopentane > 2-bromo-2-methylbutane

(ii) 1-bromo-3-methylbutane > 3-bromo-2-methylbutane > 2-bromo-2-methylbutane

(iii) 1-bromobutane > 1-bromo-3-methylbutane > 1-bromo-2-methylbutane > 1-bromo-2, 2 dimethylpropane

133. Answer the following. ISC 2002

(i) Haloalkanes easily dissolve in organic solvents. Why?

(ii) Iodoform has antiseptic properties. Give one reason to support it.

(iii) Of the two bromo derivatives, $C_6H_5CH(CH_3)Br$ and $(C_6H_5)CH(C_6H_5)Br$, which one is more reactive towards SN 1 substitution reaction and why?

Ans :

(i) Haloalkanes easily dissolve in organic solvents because both are covalent in nature (like dissolves like).
Also, the steric effect in haloalkanes is not more as seen in the case of haloarenes.

(ii) The antiseptic properties of iodoform is due to free I_2, which is liberated when iodoform comes in contact with skin.

$$4CHI_3 + 5O_2 \xrightarrow[\text{Air, }\Delta]{\text{Moisture}} 6I_2 + 4CO_2 + 2H_2O$$

(iii) The carbocation intermediate from $(C_6H_5)CH(C_6H_5)Br$ is more stable because it is stabilised by two phenyl groups due to resonance, so $(C_6H_5)CH(C_6H_5)Br$ is more reactive towards S_N1 reaction.

134. Give reasons for the following. ISC 2010

(i) Ethyl iodide undergoes S_N2 reaction faster than ethyl bromide.

(ii) (±) 2-butanol is optically inactive.

(iii) C—*X* bond length in halobenzene is smaller than C—*X* bond length in CH_3—*X*.

Ans :

(i) Iodide ion is a better leaving group because of its larger size than bromide ion, therefore ethyl iodide undergoes S_N2 reaction faster than ethyl bromide.

(ii) (±) 2-butanol is a racemic mixture. It is a mixture which contains two enantiomers in equal proportion and thus, have zero optical rotation. Therefore, it is optically inactive.

(iii) In chlorobenzene, the lone pair of electrons present on Cl-atom are in conjugation with n-electrons of the benzene ring.
As a result, $C-Cl$ bond acquires some double bond character while in CH_3-Cl, bond is a pure single bond. Since, bond length of $C-Cl$ single bond is greater than $C-Cl$ partial double bond. Therefore, $C-Cl$ bond in halobenzene is shorter than that in CH_3-Cl.

135. How would you differentiate between S_N1 and $S_N2$mechanism of substitution reactions? Give one example of each. ISC 2006

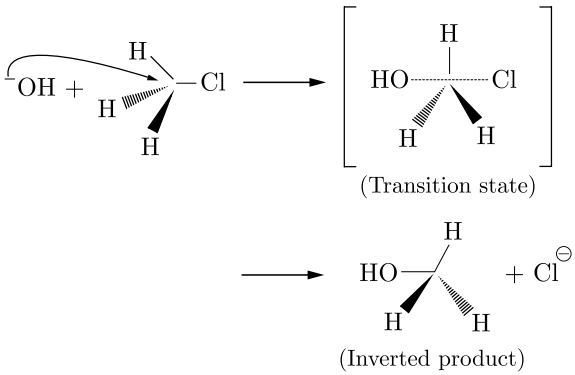
Ans :

In S_N1 mechanism of substitution reaction, the rate of reaction depends upon the concentration of only one reactant, e.g. in the reaction between *tert*-butyl bromide and hydroxide ion to form *tert*-butyl alcohol, rate of reaction depends only on the concentration of *tert*-butyl bromide.

$$(CH_3)_3C-Br + OH^- \longrightarrow (CH_3)_3C-OH + Br^-$$

It involves the formation of carbocation intermediate and racemisation.

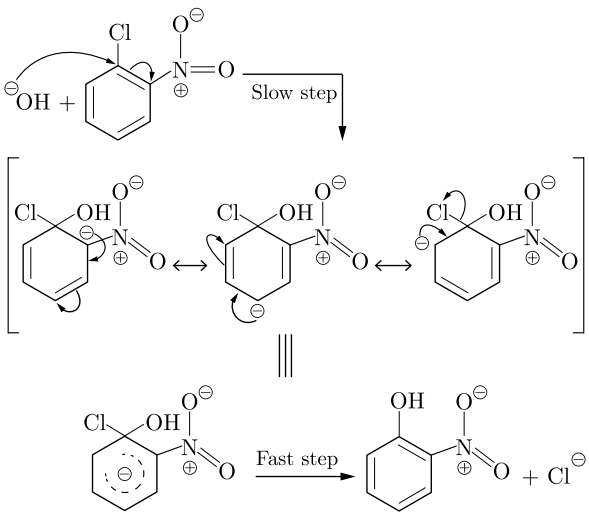
In S_N2 mechanism of substitution reaction, the rate of reaction depends upon the concentration of both the reactants. e.g. In the reaction between methyl chloride and hydroxide ion to form methanol, rate of reaction depends on the concentration of both the reactants.



It involves the formation of transition state and inversion (Walden inversion) of configuration.

NODIA

Attack at *o*-position



From the above resonating structures, it is very clear that electron density is rich at *ortho* and *para*-positions. So, presence of EWG will facilitate nucleophilic attack at *ortho* and *para*-positions.

CASE BASED QUESTIONS

A student was performing hydrolysis of optically active 2-bromobutane using aqueous potassium hydroxide in the laboratory. After completion of the reaction, the product obtained was found to be optically inactive even though the original compound was optically active. The chemistry teacher explained that the reaction proceeds through formation of an unstable intermediate which allows attack of nucleophile from different directions. The teacher further added that this behaviour is commonly observed in tertiary and some secondary haloalkanes undergoing nucleophilic substitution.

156. (i) Name the mechanism involved in the above reaction.
(ii) Which intermediate is formed during the reaction?
(iii) Why does the nucleophile attack from both sides of the intermediate?
(iv) Explain why the final product becomes optically inactive.

Ans :
(i) S_N1 mechanism.
(ii) Carbocation intermediate.
(iii) The carbocation intermediate formed is planar in shape and therefore the nucleophile can attack from either side with almost equal probability.
(iv) Attack from both sides forms equal amounts of two enantiomers. Since the two enantiomers rotate plane polarised light equally in opposite directions, the mixture becomes optically inactive due to racemisation.

157. A student heated 2-bromobutane with alcoholic KOH under reflux conditions. After the reaction, two different alkenes were obtained. On analysis, but-2-ene was found to be the major product while but-1-ene was formed only in small amount. The teacher explained that elimination reactions of haloalkanes generally follow a rule related to the stability of the alkene formed. The stability of alkene depends upon the number of alkyl groups attached to the double bonded carbon atoms.
(i) Name the type of reaction taking place in the above process.
(ii) Which reagent favours elimination reaction in haloalkanes?
(iii) State the rule governing the formation of the major alkene product.
(iv) Explain why but-2-ene is formed as the major product.

Ans :
(i) Elimination or dehydrohalogenation reaction.
(ii) Alcoholic KOH.
(iii) Saytzeff's rule.
(iv) But-2-ene contains a more substituted double bond and is therefore more stable due to greater hyperconjugation and inductive effect. Hence it is formed as the major product during elimination reaction.

158. A chemist compared the reactivity of chlorobenzene and ethyl chloride towards hydrolysis using aqueous sodium hydroxide. Ethyl chloride readily formed alcohol whereas chlorobenzene remained almost unaffected even after prolonged heating. The chemist explained that the difference in behaviour arises because of resonance effects operating in aromatic halides. In aromatic compounds, the carbon-halogen bond behaves differently from the corresponding bond in aliphatic haloalkanes.
(i) Which compound undergoes hydrolysis more readily?

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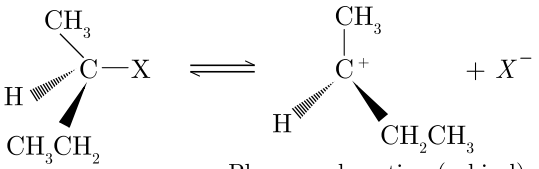
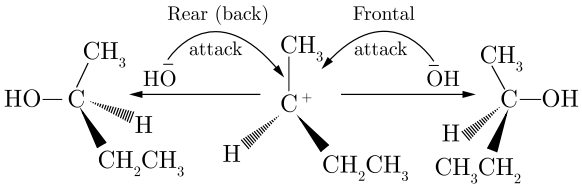
delocalisation of lone pair of electrons of the Cl-atom over the benzene ring, C – Cl bond is shorter than C – Cl bond of cyclohexyl chloride.
Since, dipole moment is a product of charge and distance, therefore, chlorobenzene has lower dipole moment than cyclohexyl chloride due to lower magnitude of negative charge on the Cl-atom and shorter C – Cl distance.]

(iii) In S_N1 reactions, if the alkyl halide is optically active, the product obtained is a racemic mixture. The intermediate carbocation formed in slowest step being sp^2-hybridised is planar (achiral) species.
Therefore, the attack of the nucleophile on it, can occur from both the faces (front and back) with equal ease, forming a 50:50 mixture of two enantiomers, i.e. the products with opposite configuration. Thus, S_N1 reaction of optically active alkyl halides are accompanied by racemisation.
e.g.



Planar carbocation (achiral)



(+)-butan-2-ol (50%) (Planar carbocation) (–)-butan-2-ol (50%)

155. Give reasons. ISC 2021

(i) *n*-butyl bromide has higher boiling point than t-butyl bromide.

(ii) Racemic mixture is optically inactive.

(iii) The presence of nitro group (—NO_2) at *o*/*p*-positions increases the reactivity of haloarenes towards nucleophilic substitution reactions.

Ans :

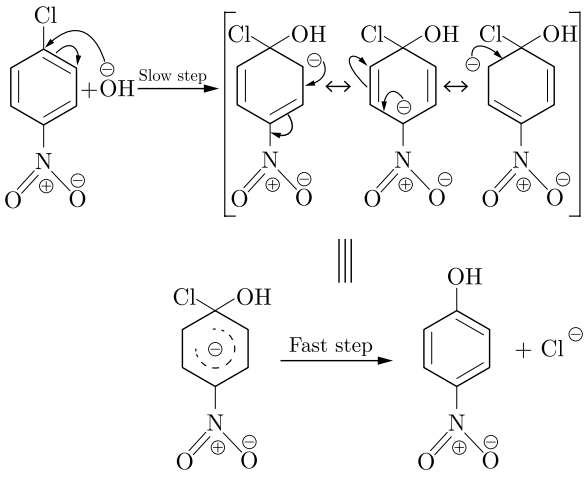
(i) Boiling point of a compound depends upon the surface area. Higher the surface area, higher will be the boiling point of a compound. Surface area decreases with increase in branching. If the compound has branching, its boiling point will be minimum. That's why, *n*-butyl bromide being (bp 375 K), a straight chain alkyl halide has higher boiling point than tertiary butyl bromide (346 K) which is a highly branched alkyl halide.

(ii) A mixture containing two enantiomers in equimolar amounts have zero optical rotation, as the rotation caused by the molecules of one isomer (enantiomer) is exactly cancelled by an equal and opposite rotation caused by the same number of molecules of other isomer (enantiomer).
Such a mixture is known as racemic mixture. Since, enantiomers have equal and opposite specific rotations, a racemic mixture exhibits no optical activity.

(iii) The reactivity of haloarenes towards nucleophilic substitution reactions can be increased by the presence of an electron withdrawing group ($-NO_2$) at *ortho* and *para*-positions. This is because NO_2 groups at *ortho* and *para*-positions withdraw electron density from the benzene ring and thus, facilitates the nucleophilic attack on haloarenes.

The mechanism can be shown as:

Attack at *p*-position



162. A chemist studied the optical behaviour of 2-bromobutane and found that it existed in two forms which were non-superimposable mirror images of each other. One form rotated plane polarised light towards the right while the other rotated it towards the left. The chemist further prepared an equimolar mixture of the two forms and observed that the mixture became optically inactive.

(i) What are such mirror image isomers called?
(ii) What type of carbon atom is present in 2-bromobutane?
(iii) What is an equimolar mixture of the two enantiomers called?
(iv) Why does the equimolar mixture become optically inactive?

Ans :

(i) Enantiomers.
(ii) Asymmetric or chiral carbon atom.
(iii) Racemic mixture.
(iv) The two enantiomers rotate plane polarised light equally in opposite directions. Their optical rotations cancel each other completely, making the mixture optically inactive.

163. A reaction mixture containing methyl bromide and sodium metal in dry ether was heated carefully. After completion of the reaction, ethane was obtained as the major product. The teacher explained that this reaction is commonly used for preparation of higher alkanes and involves coupling of alkyl groups in the presence of sodium metal.

(i) Name the reaction taking place in the above process.
(ii) Which solvent is generally used in this reaction?
(iii) Write the balanced chemical equation for the reaction.
(iv) Mention one limitation of Wurtz reaction.

Ans :

(i) Wurtz reaction.
(ii) Dry ether.
(iii) $2CH_3Br + 2Na \xrightarrow{\text{dry ether}} CH_3 - CH_3 + 2NaBr$
(iv) Wurtz reaction is not suitable for preparation of unsymmetrical alkanes because a mixture of products is formed.

164. A student prepared two compounds: $CH_2Cl - CH_2Cl$ and $CH_3 - CHCl_2$. Both compounds contained two chlorine atoms but showed different structural arrangements. The teacher explained that dihalides are classified on the basis of the relative positions of halogen atoms in the molecule.

(i) Which compound represents a vicinal dihalide?
(ii) Which compound represents a geminal dihalide?
(iii) On what basis are vicinal and geminal dihalides classified?
(iv) State one method for preparation of vicinal dihalides.

Ans :

(i) $CH_2Cl - CH_2Cl$
(ii) $CH_3 - CHCl_2$
(iii) They are classified on the basis of the position of halogen atoms in the molecule.
(iv) Vicinal dihalides are commonly prepared by addition of halogens across the double bond of alkenes.

165. An environmental scientist studied the harmful effects of DDT on living organisms. It was observed that DDT remains in the environment for a very long period and accumulates progressively in the fatty tissues of animals. The concentration of DDT increases at higher trophic levels of the food chain causing ecological imbalance and toxicity in birds and aquatic organisms.

(i) Expand the term DDT.
(ii) Why is DDT considered non-biodegradable?
(iii) In which tissues of animals is DDT mainly deposited?
(iv) Mention one environmental problem caused by accumulation of DDT.

Ans :

(i) Dichloro Diphenyl Trichloroethane.
(ii) DDT is chemically very stable and does not decompose easily by natural biological processes.
(iii) Fatty tissues.
(iv) DDT undergoes biomagnification in the food chain causing ecological imbalance and toxic effects in living organisms.

NODIA

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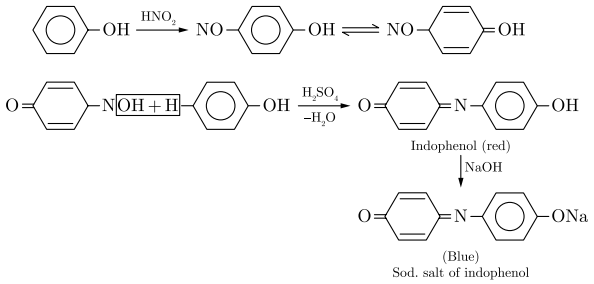
(vii) **Libermann's Test :** It is a test reaction of phenol.



3. ETHER

These are the organic compounds having general formula $C_nH_{2n+2}O$ and represented by general structure R-O-R.

They are dialkyl derivatives of water or monoalkyl derivatives of alcoholas.

3.1 General Methods of Preparation of Ethers

General methods of preparation of Ethers are as follows :

1. **From Alkyl Halides (Williamson's synthesis) (Named Reaction) :**

$$R - O - Na + R' - X \longrightarrow R - O - R' + NaX$$

2. **From Alcohols (Dehydration) :**

$$2CH_3CH_2OH \xrightarrow[Al_2O_3]{523\ K} C_2H_5OC_2H_5 + H_2O$$

Physical properties of Ethers are as follows :

1. Boiling point of ethers are much lower than those of alcohols due to lack of H-bonding.
2. Ethers are polar molecules.
3. Ethers are soluble in water due to H-bonding.

3.2 Chemical Properties of Ethers

Chemical properties of Ethers are as follows :

1. **Reaction of Ethereal Oxygen Atom :**

(i) **With cold, conc.** H_2SO_4 **:**

$$R-\underset{\text{(cold, conc.)}}{O-R} + H_2SO_4 \longrightarrow \underset{\text{(Oxonium ion)}}{R-\overset{+}{O}(H)-R} + HSO_4^-$$

2. **Reactions Due to the Cleavage of C-O Bond :**

(i) **With HX : (HBr, HI)**

$$R - O - R + 2HX \longrightarrow 2RX + H_2O$$

(ii) **With Dilute** H_2SO_4 **:**

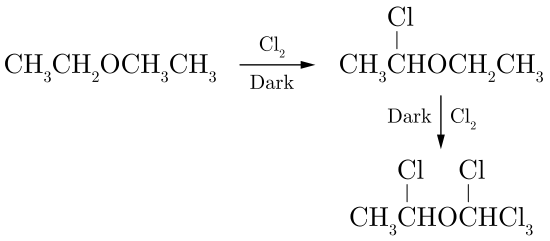
$$R - O - R + H_2O \xrightarrow[\Delta]{Dil.H_2SO_4} 2ROH$$

(iii) **With** PCl_5 **:**

$$R - O - R + PCl_5 \xrightarrow{\Delta} 2RCl + POCl_3$$

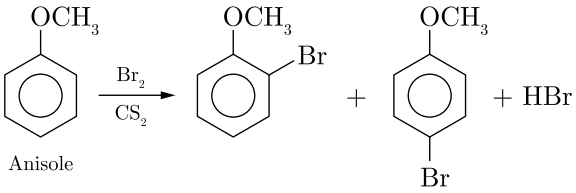
3. **Reaction of Alkyl Group :**

(i) **Halogenation :**

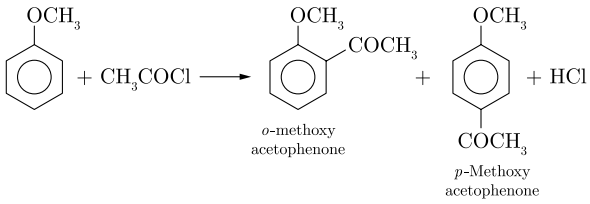


4. **Ring Substitution in Aromatic Ethers :**

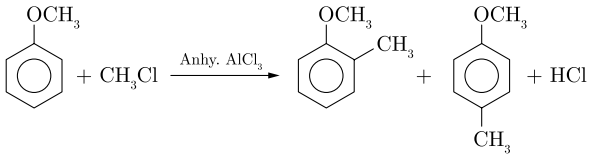
(i) **Halogenation :**



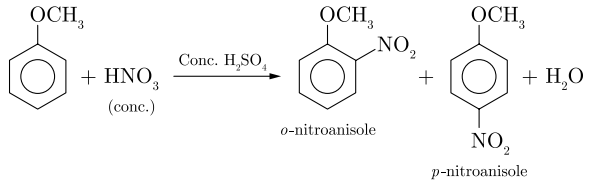
(ii) **Acylation :**



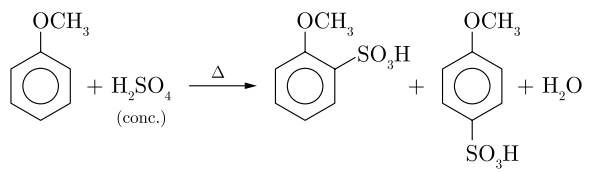
(iii) **Alkylation :**



5. **Nitration :**



6. **Sulphonation :**



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(ii) **Hydroboration-oxidation Reduction (Name Reaction) :**

$$\underset{\text{Propene}}{6CH_3-CH=CH_2} + B_2H_6 \xrightarrow{THF} 2(CH_3CH_2CH_3)_3\,B + 3H_2O_2$$

$$\xrightarrow{OH^-} 3\underset{\text{n-propyl alcohol}}{CH_3CH_2CH_2OH} + 2H_3BO_3$$

6. **From Aliphatic Primary Amines :**

$$RNH_2 + HONO \xrightarrow{NaNO_2+\text{Dil.HCl}} ROH + N_2 + H_2O$$

1.3 Physical Properties of Alcohols

The physical properties of alcohols are as follows:

1. Lower alcohols are soluble in water due to the formation of H- Bonds with water molecule. Higher alcohols are less soluble due to higher alkyl group.
2. Boiling point and melting point of alcohols are high due to the presence of intermolecular H- bonding. But boiling point and melting point increase with the increase in molecular mass and decrease with increase in branching.

1.4 Chemical Properties of Alcohols

1. **Reactions Due to the Cleavage of RO-H Bonds :**

(i) **With Active Metals Like Na, K (Acidic Character) :**

$$2RO-H + 2Na \longrightarrow 2RONa + H_2$$

(ii) **With Carboxylic Acid :**

$$RCO\boxed{OH+H}-OR' \xrightarrow[H_2SO_4]{\text{Conc.}} 2COOR' + H_2O$$

(iii) **With RMgX :**

$$RO-\boxed{H+R}MgX \longrightarrow RH + ROMgX$$

(iv) **With Acylchloride :**

$$CH_3CO\boxed{Cl+H}-OR \xrightarrow{\text{Pyridine}} CH_3COOR + HCl$$

2. **Reactions Due to the Cleavage of R-OH Bonds :**

(i) **With HX :**

$$R-OH + HX \xrightarrow{\text{Anhydrous } ZnCl_2,\ \text{Heat}} RX + H_2O$$

(ii) **With PCl_5 :**

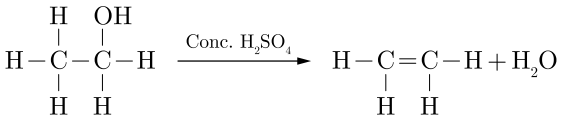
$$R-OH + PCl_5 \xrightarrow{\text{Heat}} RCl + POCl_3 + HCl$$

(iii) **With PCl_3 :**

$$3R-OH + PCl_3 \longrightarrow 3RCl + H_3PO_3$$

3. **Reactions Involving both Alkyl and Hydroxyl Groups:**

(i) **Acidic Dehydration :**



$$2CH_3CH_2OH \xrightarrow[Al_2O_3]{\Delta} C_2H_5OC_2H_5 + H_2O$$

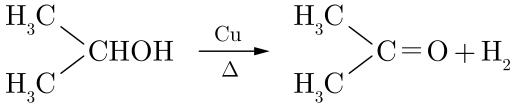
(ii) **Oxidation :**

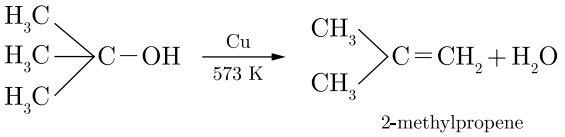
$$RCH_2OH \xrightarrow[K_2CrO_7/H^+]{[O]}$$

$$RCHO \xrightarrow[K_2CrO_7/H^+]{[O]} RCOOH$$

(iii) **Dehydrogenation :**

$$CH_3CH_2OH \xrightarrow[\Delta]{Cu} CH_3CHO + H_2$$





2-methylpropene

(iv) **With NH_3 :**

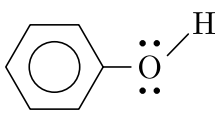
$$R-OH + NH_3 \xrightarrow[Al_2O_3]{523K} RNH_2 + H_2O$$

2. PHENOLS

These organic compounds enols are the hydroxy derivatives of arenes in which one or more $-OH$ group are directly attached to the carbon atoms of an aromatic ring.

2.1 Structure of Phenol

The -OH group in phenol is attached to sp^2 hybridised carbon of an aromatic ring.



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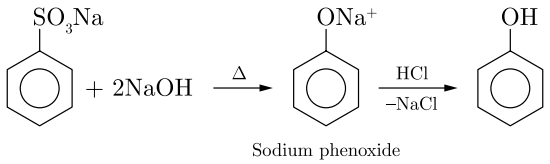
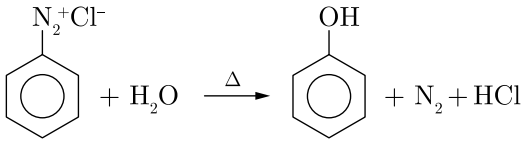
2.2 General Methods for Preparation of Phenols

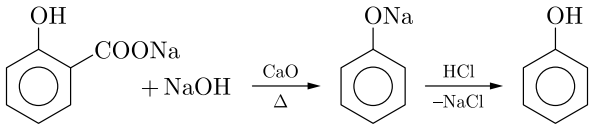
1. **From Sodium Benzene Sulphonate :**



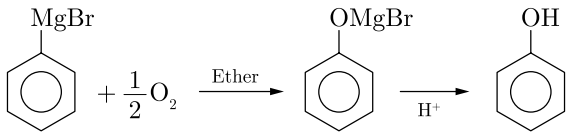
2. **From Diazonium Salts :**



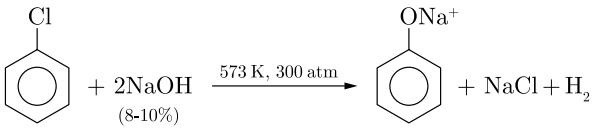
3. **From Sodium Salicylate :**

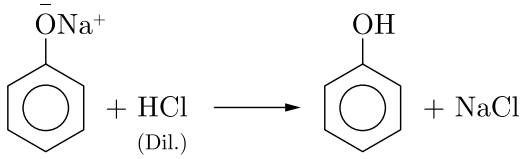


4. **From Grignard Reagent :**

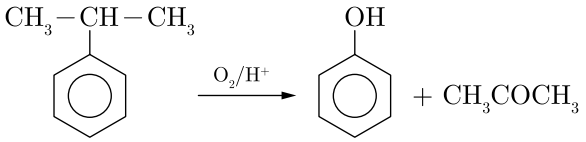


5. **Dow's Process (Name Reaction) :**





6. **From Cumene :**



2.3 Physical Properties of Phenols

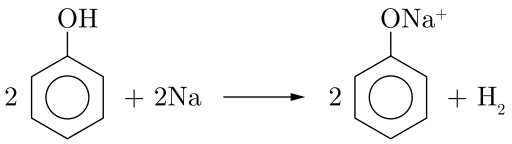
Physical properties of phenols are as follows :

1. Phenols are weakly acidic in nature but more acidic than alcohols.
2. Phenols have high boiling point due to H-bonding.
3. Phenols are slightly soluble in water.

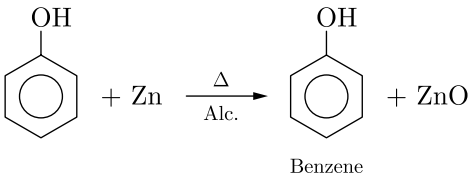
2.4 Chemical Properties of Phenols

1. **Reactions of -OH Group :**

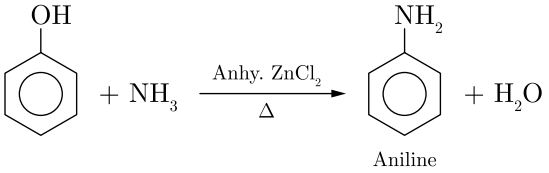
(i) **With Active Metals like Na, K :**



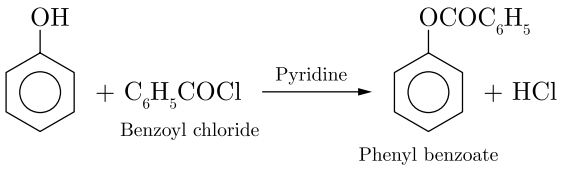
(ii) **With Zn Dust :**



(iii) **With NH_3 :**

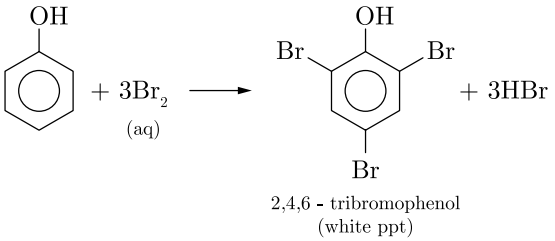


(iv) **Schotten-Baumann Reaction (Name Reaction) :**



2. **Reaction of Benzene Ring :**

(i) **Bromination :** It is a test reaction of phenol.



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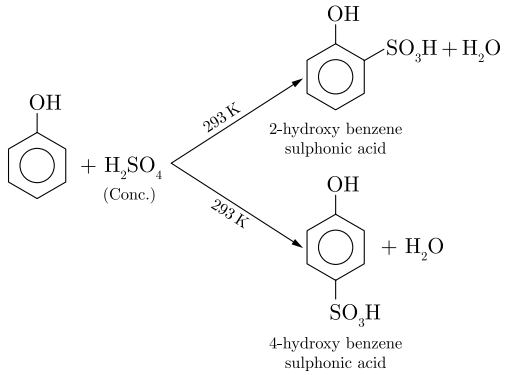
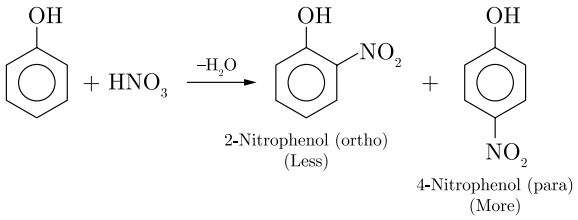
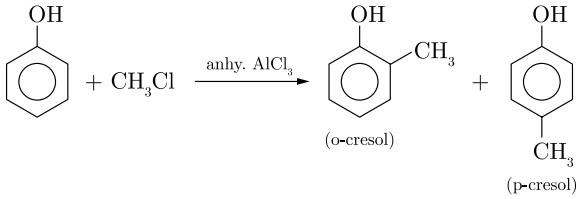
(ii) **Sulphonation :**



(iii) **Nitration :**

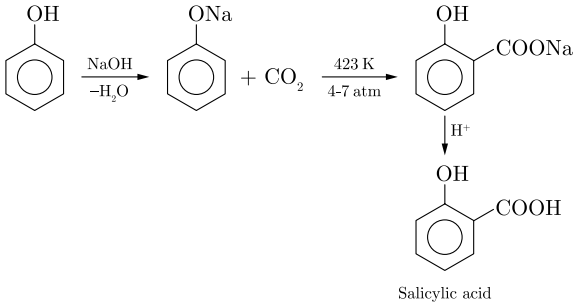


(iv) **Friedel-Craft's Reaction (Name Reaction):**

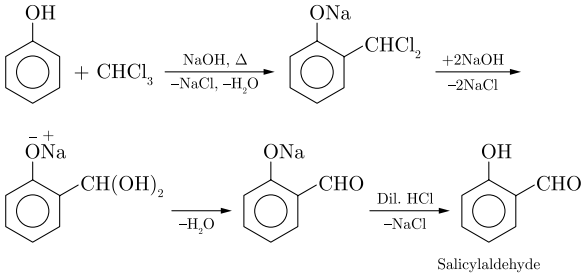


3. **Special Reactions of Phenol (Name Reaction):**

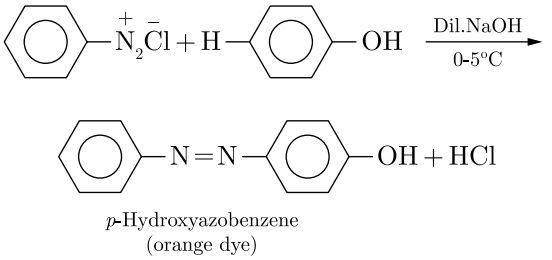
(i) **Kolbe's Reaction :**



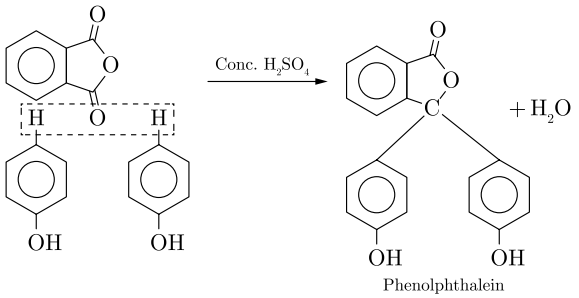
(ii) **Reimer - Tiemann Reaction (Name Reaction):**



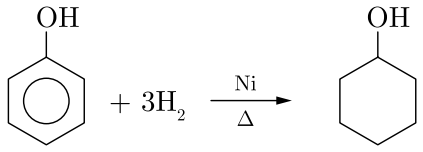
(iii) **Coupling Reaction (Name Reaction) :** It is a test reaction of phenol.



(iv) **Condensation with Phthalic Anhydride :**



(v) **Hydrogenation :**



(vi) **Action with $FeCl_3$:** It is a test reaction of phenol.

$$3C_6H_5OH + FeCl_3 \longrightarrow \underset{\text{(violet complex)}}{[Fe(OC_6H_5)_3]} + 3HCl$$

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CHAPTER 7

Alcohols, Phenols and Ethers

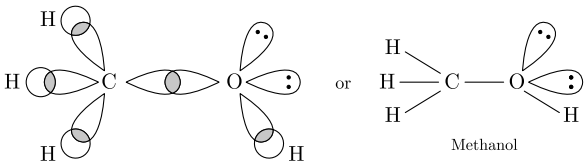
SUMMARY

1. ALCOHOLS

Hydroxy derivatives of aliphatic hydrocarbons are called alcoholes .they possess the general formula $R-OH$ where R is an alkyl or substituted alkyl group.

1.1 Structure of Alcohols

In alcohols, the oxygen of -OH group is bonded to the sp^3 hybridised carbon by a sigma bond. This bond is formed by the overlapping of sp^3 hybrid of carbon.



With One sp^3 hybrid orbital of oxygen. The remaining three sp^3 hybrid orbitals of carbon overlap with $1s$ orbitals of hydrogen. In the case of oxygen, one sp^3 hybrid orbital overlaps with $1s$ orbital of hydrogen and the remaining two sp^3 hybrid orbitals contain lone pairs of electrons.

1.2 General Methods of Preparation of Alcohols

1. **From Haloalkanes :**

$$C_2H_5Br + KOH(aq) \xrightarrow{\Delta} C_2H_5OH + KBr$$

2. **By Reduction of Aldehydes and Ketones :**

$$RCHO + H_2 \xrightarrow{Pd} RCH_2OH$$

$$RCOR' + H_2 \xrightarrow{NaBH_4} R - \underset{\displaystyle OH}{\underset{|}{CH}} - R'$$

3. **By Reduction of Carboxylic Acids and Esters:**

$$RCOOH \xrightarrow[H_2O]{LiAlH_4} RCH_2OH$$

$$RCOOR' \xrightarrow[4[H]]{Na/C_2H_5OH} RCH_2OH + R'OH$$

4. **From Grignard Reagent :**

(a) $H-\underset{\displaystyle H}{\underset{|}{C}}=O + CH_3MgBr \longrightarrow H-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle H}{\overset{|}{C}}}}-OMgBr \xrightarrow{H^+/H_2O} H-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle H}{\overset{|}{C}}}}-OH + Mg(OH)Br$

Formaldehyde — Ethyl alcohol (1° alc)

(b) $CH_3-\underset{\displaystyle H}{\underset{|}{C}}=O + CH_3MgBr \longrightarrow CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle H}{\overset{|}{C}}}}-OMgBr \xrightarrow{H^+/H_2O} CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle H}{\overset{|}{C}}}}-OH + Mg(OH)Br$

Acetaldehyde — Isopropyl alcohol (2° alc)

(c) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=O + CH_3MgBr \longrightarrow CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-OMgBr \xrightarrow{H^+/H_2O} CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-OH + Mg(OH)Br$

Acetone — Tert-butylalcohol (3° alc)

5. **From Alkenes :**

(i) **Hydration of Alkenes :**

$$\underset{\text{Ethene}}{CH_2=CH_2} + \underset{\text{(conc.)}}{H_2SO_4} \longrightarrow CH_3CH_2SO_3OH \xrightarrow{+H_2O,\ \text{boil}} CH_3CH_2OH + H_2SO_4$$

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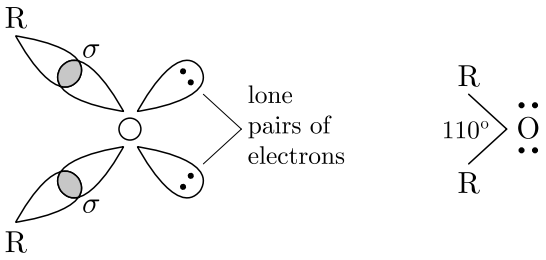
3.3 Structure of Ethers

In these compounds the functional group $(-O-)$ is bonded to two alkyl group by σ-bonds making a bond angle of 110° as:



Distinction Between 1°, 2°, 3° Alcohols :

The following tests are used :

1. Victor Meyer's test
2. Lucas test
3. Action with hot reduced copper at 573 K
4. Oxidation

Distinction Between Alcohols and Phenols :

The following tests are used :

1. Blue litmus solution used
2. Br_2 water test
3. Action with $FeCl_3$
4. Dye test.

****

OBJECTIVE QUESTIONS

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1. When phenol is treated with zinc dust, it gives
ISC 2021-22 (Sem-I)

(a) benzoic acid (b) benzaldehyde
(c) benzene (d) toluene

Ans : (c) benzene
When phenol is distilled with Zn-dust, it gives benzene. it is an example of reduction. Phenol loses one O atom.

2. When excess of ethanol is heated with conc. H_2SO_4 at 413 K, which compound is obtained?
ISC 2021-22 (Sem-I)

(a) Diethyl sulphate
(b) Ethyl hydrogen sulphate
(c) Ethoxy ethane
(d) Ethene

Ans : (d) Ethene

$$\underset{\text{Ethanol (Excess)}}{CH_3CH_2OH} \xrightarrow[443\,K]{Conc.H_2SO_4} \underset{\text{Ethene}}{CH_2=CH_2} + H_2O$$

3. Boiling point of ethyl alcohol is greater than diethyl ether due to
ISC Specimen 2021-22 (Sem-I)

(a) van der Waals' forces
(b) London forces
(c) polarity
(d) hydrogen bonding

Ans : (d) hydrogen bonding
The boiling point of ethyl alcohol is greater than diethyl ether due to hydrogen bonding.

4. Acetyl chloride on heating with diethyl ether in the presence of anhydrous $ZnCl_2$ gives
ISC 2021-22 (Sem-I)

(a) ethyl alcohol and acetic acid
(b) methyl chloride and methyl alcohol
(c) methyl acetate and methyl alcohol
(d) ethyl acetate and ethyl chloride

Ans : (d) ethyl acetate and ethyl chloride

$$\underset{\text{Acetyl chloride}}{CH_3COCl} + \underset{\text{Ethyl ether}}{C_2H_5OC_2H_5} \xrightarrow[\Delta]{\text{Anhyd. } ZnCl_2} \underset{\text{Ethyl chloride}}{C_2H_5Cl} + \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5}$$

Ans : (c) Propan-2-ol

Secondary alcohols undergo controlled oxidation to form ketones. In propan-2-ol, the hydroxyl-bearing carbon is attached to two alkyl groups, therefore oxidation removes two hydrogen atoms forming propanone. Primary alcohols form aldehydes and carboxylic acids while tertiary alcohols generally resist oxidation due to absence of hydrogen on the hydroxyl-bearing carbon.

17. In Williamson synthesis, sodium ethoxide reacts with methyl bromide to produce:

ISC 2024

(a) Ethanol

(b) Methanol

(c) Dimethyl ether

(d) Methoxyethane

Ans : (d) Methoxyethane

Williamson ether synthesis involves nucleophilic substitution between an alkoxide ion and an alkyl halide. Sodium ethoxide acts as the nucleophile and attacks methyl bromide displacing bromide ion. As a result methoxyethane is formed. This reaction is widely used for preparation of symmetrical and unsymmetrical ethers under suitable conditions.

18. Which of the following compounds gives violet coloration with neutral $FeCl_3$ solution?

ISC 2020

(a) Ethanol

(b) Diethyl ether

(c) Phenol

(d) Benzene

Ans : (c) Phenol

Phenol reacts with neutral ferric chloride solution forming a coloured ferric phenoxide complex which gives violet coloration. This reaction is commonly used as a qualitative test for phenolic hydroxyl groups. Alcohols and ethers do not produce this characteristic colour because they cannot form similar resonance stabilised complexes with ferric ions.

19. Why do alcohols possess higher boiling points than ethers of comparable molecular mass?

ISC 2014

(a) Alcohols are non-polar molecules

(b) Alcohols contain more carbon atoms

(c) Alcohols undergo intermolecular hydrogen bonding

(d) Ethers contain weaker carbon-oxygen bonds

Ans : (c) Alcohols undergo intermolecular hydrogen bonding

Alcohol molecules contain hydroxyl groups capable of forming strong intermolecular hydrogen bonds. Considerable energy is therefore required to separate alcohol molecules during boiling. Ethers lack hydrogen directly bonded to oxygen and cannot form such intermolecular hydrogen bonding efficiently. Consequently ethers possess much lower boiling points than corresponding alcohols.

20. Which named reaction converts phenol into salicylaldehyde?

ISC 2010

(a) Kolbe reaction

(b) Friedel-Crafts reaction

(c) Reimer-Tiemann reaction

(d) Williamson synthesis

Ans : (c) Reimer-Tiemann reaction

In the Reimer-Tiemann reaction, phenol reacts with chloroform in the presence of aqueous sodium hydroxide. Dichlorocarbene generated during the reaction attacks the activated benzene ring mainly at the ortho position. Subsequent hydrolysis produces salicylaldehyde as the major product, an important aromatic aldehyde used in organic synthesis.

21. During Lucas test, a student observed that one alcohol produced turbidity only after heating while another gave immediate turbidity at room temperature. Which alcohol is expected to give immediate turbidity?

ISC 2004

(a) Ethanol

(b) Propan-1-ol

(c) Propan-2-ol

(d) 2-Methylpropan-2-ol

Ans : (d) 2-Methylpropan-2-ol

In Lucas test, tertiary alcohols react immediately with concentrated HCl in the presence of anhydrous $ZnCl_2$ because they form highly stable tertiary carbocations rapidly. Consequently insoluble alkyl chlorides separate immediately producing turbidity. Secondary alcohols react slowly while primary alcohols require heating because their carbocations are comparatively unstable.

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11. Lucas reagent was added separately to ethanol, propan-2-ol and tert-butyl alcohol at room temperature. The student observed immediate turbidity only in one sample. Which alcohol showed this behaviour?

ISC 2023

(a) Ethanol

(b) Propan-1-ol

(c) Propan-2-ol

(d) Tert-butyl alcohol

Ans : (d) Tert-butyl alcohol

Lucas reagent contains concentrated HCl and anhydrous $ZnCl_2$. Tertiary alcohols react immediately because they readily form stable tertiary carbocations. Consequently alkyl chlorides are produced rapidly causing turbidity at room temperature. Primary alcohols react very slowly while secondary alcohols show turbidity only after a few minutes due to lower carbocation stability.

12. Phenol is more acidic than ethanol mainly because:

ISC 2016

(a) Ethanol contains more hydrogen atoms

(b) Phenoxide ion is resonance stabilised

(c) Ethanol forms stronger hydrogen bonds

(d) Phenol has higher molecular mass

Ans : (b) Phenoxide ion is resonance stabilised

On losing a proton, phenol forms phenoxide ion in which the negative charge is delocalised over the aromatic ring through resonance. This stabilises the conjugate base significantly. In ethanol, the ethoxide ion does not possess resonance stabilisation. Therefore proton removal from phenol occurs more easily, making phenol more acidic than ethanol.

13. Which product is formed as the major product when phenol undergoes nitration with concentrated nitric acid?

ISC 2022

(a) Nitrobenzene

(b) o-Nitrophenol

(c) p-Nitrophenol

(d) 2,4,6-Trinitrophenol

Ans : (d) 2,4,6-Trinitrophenol

The hydroxyl group in phenol strongly activates the benzene ring towards electrophilic substitution reactions. Under the action of concentrated nitric acid, nitration occurs at ortho and para positions repeatedly. Consequently three nitro groups enter the ring forming 2,4,6-trinitrophenol or picric acid as the major product.

14. During dehydration of ethanol using concentrated H_2SO_4 at 443 K, the major product formed is:

ISC 2013

(a) Ethanal

(b) Diethyl ether

(c) Ethene

(d) Acetic acid

Ans : (c) Ethene

At higher temperature (443 K) concentrated sulphuric acid acts as a dehydrating agent and removes water from ethanol. The reaction proceeds through elimination mechanism producing ethene. At lower temperature (413 K) intermolecular dehydration predominates producing ether, whereas higher temperature favours alkene formation because elimination becomes thermodynamically more favourable.

15. Which of the following reactions is used for preparation of phenol from chlorobenzene under drastic conditions?

ISC 2004

(a) Kolbe reaction

(b) Reimer-Tiemann reaction

(c) Dow's process

(d) Cumene process

Ans : (c) Dow's process

In Dow's process, chlorobenzene is heated with aqueous sodium hydroxide at high temperature and pressure forming sodium phenoxide, which on acidification produces phenol. The reaction requires drastic conditions because chlorobenzene possesses partial double bond character in the carbon-chlorine bond due to resonance, making nucleophilic substitution difficult.

16. Which alcohol on oxidation produces a ketone?

ISC 2002

(a) Methanol

(b) Ethanol

(c) Propan-2-ol

(d) 2-Methylpropan-2-ol

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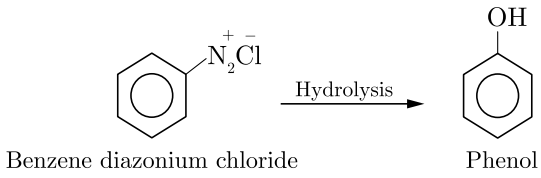
5. Benzene diazonium chloride on hydrolysis gives
ISC Specimen 2021-22 (Sem-I)

(a) benzene (b) phenol

(c) chlorobenzene (d) benzyl alcohol

Ans : (b) phenol



Benzene diazonium chloride Phenol

6. Haloform reaction does not take place with which of the following compounds?
ISC Specimen 2021-22 (Sem-I)

(a) Propanone (b) 2-propanol

(c) Ethanol (d) Methanol

Ans : (d) Methanol

Haloform reaction is shown by compounds containing the group:

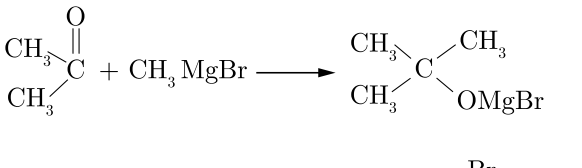
CH_3CO– (methyl ketone) or compounds that can be oxidized to form this group, such as ethanol and 2-propanol. Propanone is a methyl ketone, so it gives the haloform reaction. Ethanol and 2-propanol are oxidized to compounds containing the CH_3CO– group and also give this reaction. Methanol cannot form a methyl ketone on oxidation, so it does not undergo the haloform reaction.

7. Reaction between acetone and methyl magnesium chloride, followed by hydrolysis will give
ISC Specimen 2021-22 (Sem-I)

(a) tent-butyl alcohol (b) iso-butyl alcohol

(c) iso-propyl alcohol (d) sec-butyl alcohol

Ans : (a) tent-butyl alcohol



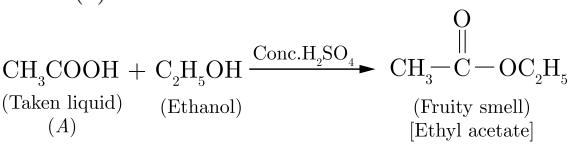
2-methyl-propan-2-ol
(*tert*-butyl alcohol)

8. A liquid is mixed with ethanol and few drops of conc. H_2SO_4 is added. A compound with a fruity smell is formed. The liquid is
ISC Specimen 2021-22 (Sem-I)

(a) HCHO (b) CH_3CHO

(c) CH_3COOH (d) CH_3COCH_3

Ans : (a) HCHO



(Taken liquid) (*A*) (Ethanol) (Fruity smell) [Ethyl acetate]

Thus, the compound (*A*) is acetic acid.

9. In the dehydration of alcohols to alkenes by heating with concentrated sulphuric acid, the initiation step is
ISC 2018

(a) formation of carbocation

(b) formation of an ester

(c) protonation of alcohol molecule

(d) elimination of water

Ans : (c) protonation of alcohol molecule

During dehydration of alcohols using concentrated sulphuric acid, the first step is the protonation of the alcohol molecule. The alcohol reacts with the acid, and the –OH group gets protonated to form $–OH_2^+$, which is a better leaving group. After this, water is eliminated and a carbocation may be formed, leading to the formation of an alkene.

10. When ethene reacts with HBr, a compound (*X*) is formed. When compound (*X*) reacts with sodium ethoxide then compound (*Y*) is formed along with sodium bromide.
ISC 2021-22 (Sem-1)

(i) Identify the compound (*X*)-

(a) C_2H_6 (b) C_2H_5Br

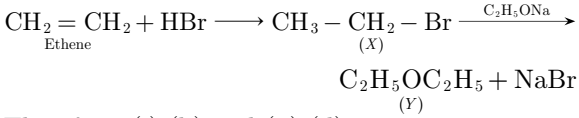
(c) CH_3Br (d) $C_2H_4Br_2$

(ii) Identify the compound (*Y*)-

(a) CH_3OH (b) C_2H_5OH

(c) CH_3OCH_3 (d) $C_2H_5OC_2H_5$

Ans :



Ethene (*X*) (*Y*)

Therefore, (i)-(b) and (ii)-(d) are correct.

NODIA

22. A student treated phenol with bromine water and observed formation of a white precipitate without using any catalyst. Which property of phenol is mainly responsible for this reaction?

ISC 2014

(a) Weak acidic nature of phenol

(b) Resonance stabilisation of benzene ring

(c) Activating effect of hydroxyl group

(d) Presence of intermolecular hydrogen bonding

Ans : (c) Activating effect of hydroxyl group

The hydroxyl group attached to the benzene ring donates electron density through resonance and strongly activates the ring towards electrophilic substitution reactions. As a result bromination occurs readily at ortho and para positions even in absence of catalyst producing white precipitate of 2,4,6-tribromophenol instantly.

23. When acetaldehyde is treated with Grignard reagent followed by hydrolysis, the product formed is

ISC 2015, 2018

(a) primary alcohol

(b) secondary alcohol

(c) carboxylic acid

(d) tertiary alcohol

Ans : (b) secondary alcohol

$$CH_3-CHO + RMgX \xrightarrow[(ii)\ H_2O/H^+]{(i)\ \text{Dry ether}} H_3C-\underset{\underset{R}{|}}{\overset{\overset{H}{|}}{C}}-OH + Mg(OH)X$$

Secondary alcohol (2°)

24. Which of the following reactions correctly explains the acidic nature of alcohols?

ISC 2025

(a) Reaction with concentrated H_2SO_4

(b) Reaction with sodium metal liberating hydrogen gas

(c) Reaction with PCl_5

(d) Dehydration to form alkene

Ans : (b) Reaction with sodium metal liberating hydrogen gas

Alcohols possess weak acidic character because they can donate the hydrogen atom of the hydroxyl group. When alcohol reacts with sodium metal, sodium alkoxide and hydrogen gas are produced.

$2ROH + 2Na \rightarrow 2RONa + H_2$

Evolution of hydrogen confirms the acidic behaviour of alcohols.

25. While comparing boiling points, a student observed that ethanol has much higher boiling point than dimethyl ether although both possess same molecular mass. The main reason is:

ISC 2023

(a) Ethanol contains double bond

(b) Ether molecules are heavier

(c) Ethanol undergoes intermolecular hydrogen bonding

(d) Ether molecules are ionic in nature

Ans : (c) Ethanol undergoes intermolecular hydrogen bonding

Ethanol molecules are associated through strong intermolecular hydrogen bonding due to the presence of hydroxyl group. Large amount of energy is required to break these interactions during boiling. Dimethyl ether cannot form intermolecular hydrogen bonding because it lacks hydrogen directly attached to oxygen, therefore its boiling point remains much lower.

26. During oxidation reactions, which alcohol resists oxidation under ordinary conditions due to absence of hydrogen atom on the carbon attached to hydroxyl group?

ISC 2006

(a) Propan-1-ol

(b) Propan-2-ol

(c) 2-Methylpropan-2-ol

(d) Ethanol

Ans : (c) 2-Methylpropan-2-ol

Oxidation of alcohols generally requires removal of hydrogen atom from the carbon bearing the hydroxyl group. Tertiary alcohols like 2-methylpropan-2-ol do not contain such hydrogen atoms. Consequently oxidation becomes difficult under ordinary conditions and tertiary alcohols resist oxidation unlike primary and secondary alcohols.

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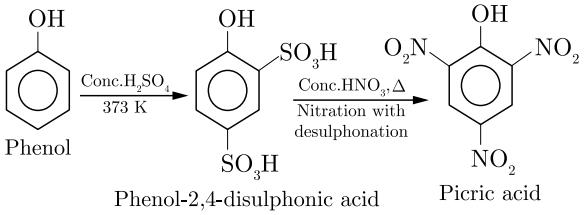
64. How will you convert phenol to picric acid? Write the relevant equation.

ISC 2003

Ans :

Picric acid from phenol Phenol is treated with conc. HNO_3 and conc. H_2SO_4 to yield 2, 4, 6-trinitrophenol (picric acid).

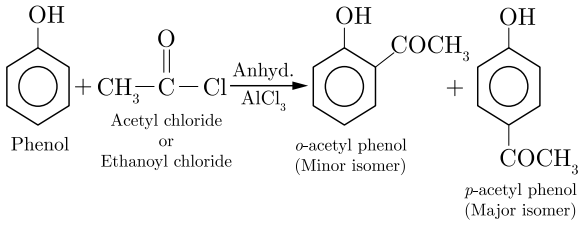


65. Write the equation and name the following reaction. Phenol with acetyl chloride in the presence of $AlCl_3$.

ISC 2004

Ans :

Phenol when treated with acetyl chloride in the presence of $AlCl_3$ to give the mixture of *o*- and *p*-derivatives.



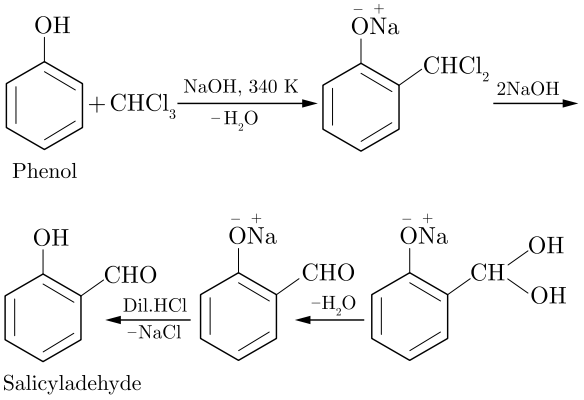
66. Write chemical equations to illustrate the following name reaction.

Reimer-Tiemann reaction

ISC 2020

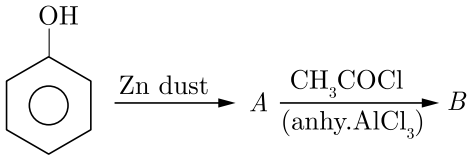
Ans :

Reimer-Tiemann reaction

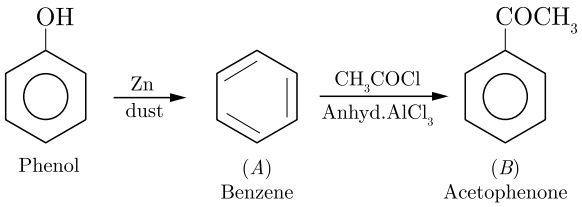


67. Identify the compounds A and B in the given reaction.

ISC 2022



Ans :



68. Give one chemical test each to distinguish between the following pairs of compounds :

ISC 2020, 2016

(i) Ethanol and dimethyl ether

ii) Diethyl ether with phosphorus pentachloride.

Ans :

(i) Ethyl alcohol gives yellow precipitate during iodoform test, while dimethyl ether does not give such test.

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} + 6NaOH + 4I_2 \longrightarrow CHI_3(\downarrow) + HCOO^-Na^+ + 5NaI + 5H_2O$$

$$\underset{\text{Dimethyl ether}}{CH_3-O-CH_3} + 6NaOH + 4I_2 \longrightarrow \text{No reaction}$$

(ii) $\underset{\text{Diethyl ether}}{C_2H_5-O-C_2H_5} + PCl_5 \xrightarrow{\Delta} \underset{\text{Ethyl chloride}}{2C_2H_5Cl} + \underset{\text{Phosphoryl chloride}}{POCl_3}$

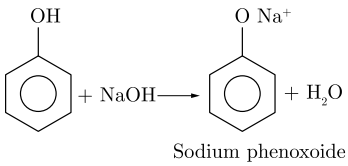
69. Give balanced chemical equations for the following reaction. Phenol is treated with ice cold alkaline solution of benzene diazonium chloride.

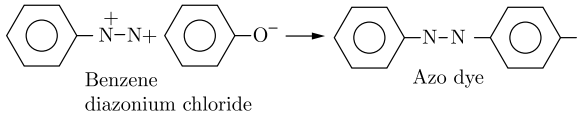
ISC 2025, 2020

Ans :

Phenol is treated with ice cold alkaline solution of benzene diazonium chloride to give orange-yellow Azo dye ($N = N$ linkage) compound.

Coupling reaction :





32. The reaction

Sodium alkoxide + alkyl halide ⟶ ether + sodium halide is called

ISC Specimen 2021-22 (Sem-I)

(a) Wurtz reaction

(b) Kolbe's reaction

(c) Perkin's reaction

(d) Williamson's synthesis

Ans : (d) Williamson's synthesis

In Williamson's ether synthesis, a sodium alkoxide reacts with an alkyl halide to form an ether and sodium halide.

General reaction:

RONa + R'X → ROR' + NaX

where:

RONa = sodium alkoxide

R'X = alkyl halide

ROR' = ether

This reaction is widely used for the preparation of symmetrical as well as unsymmetrical ethers.

33. Phenol and ethyl alcohol can be distinguished by a single chemical test.

ISC 2021-22 (Sem-I)

(i) Which of the following is the reagent used to distinguish phenol from ethyl alcohol?

(a) Solid PCl_5

(b) Dry sodium metal

(c) Neutral $FeCl_3$

(d) Acetyl chloride in presence of pyridine

(ii) Which colour is developed in the solution due to the addition of the above reagent to phenol?

(a) Blue (b) Green

(c) Red (d) Violet

Ans :

(i) (c) Neutral $FeCl_3$

Phenol react with Fe^{3+} ion in a ferric chloride ($FeCl_3$) solution to give complex ions with strong colours from red to purple. Ethanol doesn't undergo such reaction.

(ii) (d) Violet

Violet colour is developed in solution due to addition of phenol to $FeCl_3$.

34. When phenol is treated with excess of bromine water, a white precipitate is formed. The compound formed is

ISC 2021-22 (Sem-I)

(a) *m*-bromophenol

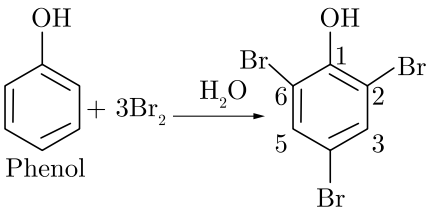
(b) *o*- and *p*-bromophenol

(c) 3,5-dibromophenol

(d) 2,4,6-tribromophenol

Ans : (d) 2,4,6-tribromophenol

Phenol reacts readily with bromine water because the –OH group activates the benzene ring towards electrophilic substitution. When excess bromine water is added, bromine atoms enter the ortho and para positions of the ring. As a result, 2,4,6-tribromophenol is formed as a white precipitate. This reaction is commonly used as a test for phenol..



2,4,6- tribromophenol

35. Chlorobenzene is fused with aqueous sodium hydroxide at 623 K and 300 atm followed by hydrolysis with dil. HCl.

ISC 2021-22 (Sem-I)

(i) The organic product formed is

(a) phenol

(b) sodium phenoxide

(c) benzene

(d) cyclohexyl chloride

(ii) What is the name of the above reaction?

(a) Williamson's synthesis

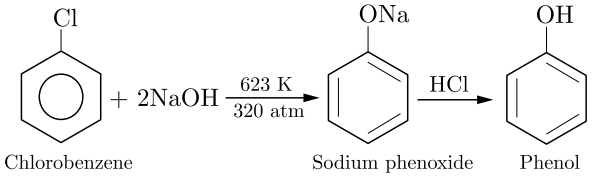
(b) Dow's process

(c) Rosenmund's reduction

(d) Kolbe's reaction

Ans :

(i) (a) phenol



(ii) (b) Dow's process

The name of this reaction is Dow's process.

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27. In Williamson ether synthesis, why are primary alkyl halides generally preferred over tertiary alkyl halides?

ISC 2001

(a) Primary alkyl halides are more acidic

(b) Tertiary alkyl halides undergo elimination reactions readily

(c) Primary alkyl halides are insoluble in ether

(d) Tertiary alkyl halides form weaker carbon-halogen bonds

Ans : (b) Tertiary alkyl halides undergo elimination reactions readily

Williamson ether synthesis proceeds through nucleophilic substitution mechanism. Primary alkyl halides favour substitution because steric hindrance is minimum. Tertiary alkyl halides, however, readily undergo elimination reactions in presence of strong bases such as alkoxides, producing alkenes instead of ethers. Hence primary alkyl halides are preferred for successful ether synthesis.

28. A student added neutral ferric chloride solution separately to ethanol and phenol. Only one compound produced violet coloration. This observation confirms:

ISC 2010

(a) Presence of carbonyl group

(b) Presence of phenolic hydroxyl group

(c) Presence of aldehyde group

(d) Presence of ether linkage

Ans : (b) Presence of phenolic hydroxyl group

Phenol reacts with neutral ferric chloride forming a coloured ferric phenoxide complex which produces violet coloration. This reaction is a characteristic test for phenolic hydroxyl groups. Ordinary alcohols such as ethanol do not form similar complexes with ferric ions and therefore fail to produce the characteristic violet colour.

29. In Reimer-Tiemann reaction, the electrophile responsible for formylation of phenol is:

ISC 2017

(a) CO_2

(b) $CHCl_2^+$

(c) Dichlorocarbene

(d) Formyl chloride

Ans : (c) Dichlorocarbene

In the Reimer-Tiemann reaction, chloroform reacts with aqueous sodium hydroxide producing dichlorocarbene ($:CCl_2$) as the reactive intermediate. This electrophile attacks the activated benzene ring of phenol mainly at the ortho position. Subsequent hydrolysis converts the intermediate into salicylaldehyde, an aromatic aldehyde containing hydroxyl and formyl groups.

30. Which statement correctly explains why phenol undergoes electrophilic substitution more readily than benzene?

ISC 2024

(a) Phenol is non-aromatic

(b) Oxygen withdraws electrons completely

(c) Hydroxyl group increases electron density in benzene ring

(d) Phenol forms ionic bonds easily

Ans : (c) Hydroxyl group increases electron density in benzene ring

The hydroxyl group attached to benzene ring donates electron density through resonance effect. Electron density particularly increases at ortho and para positions making the aromatic ring highly reactive towards electrophiles. Consequently phenol undergoes bromination, nitration and sulphonation much more readily than ordinary benzene under mild conditions.

NODIA

31. During preparation of alcohols from Grignard reagents, why must the reaction be carried out under anhydrous conditions?

ISC 2025

(a) Water converts alcohol into alkene

(b) Water destroys Grignard reagent immediately

(c) Water acts as catalyst

(d) Water oxidises magnesium metal

Ans : (b) Water destroys Grignard reagent immediately

Grignard reagents are highly reactive organometallic compounds and behave as strong bases. Even traces of moisture react with them producing hydrocarbons and rendering the reagent ineffective.

$RMgX + H_2O \rightarrow RH + Mg(OH)X$

Therefore all apparatus and solvents used during Grignard reactions must be completely dry.

(b) Both assertion and reason are correct but reason is not the correct explanation of assertion.

(c) Assertion is correct and reason is incorrect.

(d) Assertion is incorrect and reason is correct.

ISC 2021-22 (Sem-I)

Ans : (a) Both assertion and reason are correct and reason is the correct explanation of assertion.

Phenol reacts with neutral ferric chloride to form a violet coloured solution. This colour appears due to the formation of a complex ion between phenol and ferric ions . The reaction is commonly used as a test for phenol.

40. **Assertion (A)** Ethers are more volatile than alcohols having the same molecular formula.

Reason (R) Alcohols have intermolecular hydrogen bond.

ISC Specimen 2021-22 (Sem-I)

(a) Both assertion and reason are correct and reason is the correct explanation of assertion.

(b) Both assertion and reason are correct but reason is not the correct explanation of assertion.

(c) Assertion is correct and reason is incorrect.

(d) Assertion is incorrect and reason is correct.

Ans : (b) Both assertion and reason are correct but reason is not the correct explanation of assertion.

Alcohols contain an –OH group due to which they form strong intermolecular hydrogen bonds. These hydrogen bonds increase the boiling point and decrease volatility. Ethers do not form such strong intermolecular hydrogen bonding, so they have lower boiling points and are more volatile than alcohols having the same molecular formula.

FILL IN THE BLANK

41. The primary alcohols are easily oxidised first into _____and then into _____ .

ISC 2023

Ans :

Aldehyde, Carboxylic acid

42. _____ and _____ are functional isomers.

ISC 2009

Ans :

Ethanol, dimethyl ether

43. The acidic strength of phenol is _____ ethyl alcohol but _____ nitrophenol.

ISC Specimen 2018

Ans :

greater than, less than.

44. Sodium phenoxide reacts with methyl chloride to give_____ The reaction is known as _____

ISC Specimen 2023

Ans :

Anisole, Williamson's synthesis

45. A mixture of conc. HCl and anhydrous $ZnCl_2$ is called _____ which shows maximum reactivity with _____ alcohol.

ISC 2019

Ans :

Lucas reagent, tertiary

46. _____ is an example of trihydric alcohol and _____ is an example of dihydric alcohol.

ISC 2011

Ans :

Glycerol is an example of trihydric alcohol and glycol is an example of dihydric alcohol.

47. _____ and _____ are functional isomers.

ISC 2009

Ans :

The isomer which differs by the presence of functional group are called functional isomerism.

Ethanol and diethyl ether are functional isomers.

48. Propan-2-ol on reaction with iodine and sodium hydroxide gives _____ precipitate and the reaction is called _____ test.

ISC 2018

Ans :

Propan-2-ol on reaction with iodine and sodium hydroxide gives yellow precipitate and the reaction is called iodoform test.

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36. An unknown alcohol is treated with Lucas reagent to determine whether the alcohol is primary, secondary or tertiary.

ISC Specimen 2021-22 (Sem-I)

(i) Which alcohol reacts fastest and by what mechanism?

(a) Tertiary alcohol by S_N2

(b) Secondary alcohol by S_N1

(c) Tertiary alcohol by S_N1

(d) Secondary alcohol by S_N2

(ii) What is the chemical composition of the Lucas reagent used above?

(a) Anhydrous zinc chloride in concentrated HCl

(b) Anhydrous aluminium chloride in concentrated HCl

(c) Anhydrous lead chloride in concentrated HCl

(d) Anhydrous barium chloride in concentrated HCl

Ans :

(i) (c) Tertiary alcohol by S_N1
Tertiary alcohol reacts fastest and by S_N1 mechanism.

(ii) (a) Anhydrous zinc chloride in concentrated HCl
Anhydrous zinc chloride in concentrated HCl is used as Lucas reagent.

37. Phenol is heated with alcoholic KOH and chloroform.

ISC 2021-22 (Sem-I)

(i) What is the name of the reaction?

(a) Cannizzaro reaction

(b) Gattermann reaction

(c) Reimer - Tiemann reaction

(d) Kolbe reaction

(ii) What is the main product formed in this reaction?

(a) Salicylaldehyde

(b) Salicylic acid

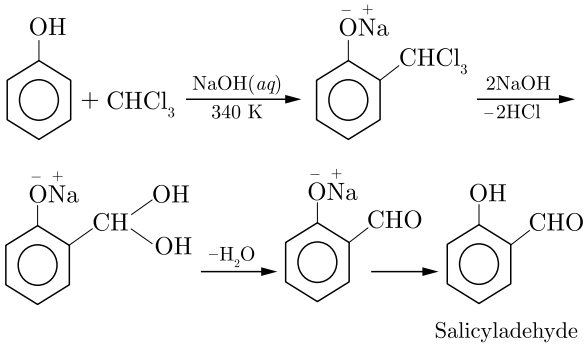
(c) Aniline

(d) Phenyl isocyanide

Ans :

(i) (c) Reimer - Tiemann reaction
The name of given reaction is Reimer-Tiemann reaction.

(ii) (a) Salicylaldehyde



Salicyladehyde

38. Conversion of chlorobenzene into phenol.

(i) Which of the following statements is correct for the above conversion?

ISC 2021-22 (Sem-I)

(a) Heating it with alc. KOH at room temperature.

(b) Heating it with aqueous NaOH at 623 K under pressure followed by acidificatioin with dilute HCl.

(c) Heating it with CuCN followed by acidification with dilute HCl.

(d) Heating it with sodium metal in the presence of dry ether.

(ii) What is the name of the above reaction?

(a) Dow process

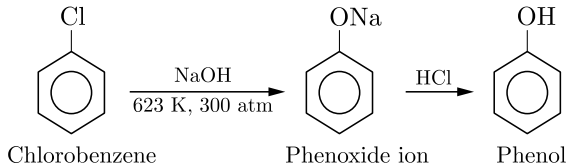
(b) Wurtz reaction

(c) Sandmeyer's reaction

(d) Kolbe's reaction

Ans :

(i) (b)
The conversion given in option (b) is incorrect.



Chlorobenzene Phenoxide ion Phenol

(ii) (a)
The name of given reaction is Dow's process.

39. **Assertion (A)** Phenol reacts with neutral ferric chloride ($FeCl_3$) and gives violet colour solution.

Reason (R) The violet colour solution is due to the formation of $[Fe(OC_6H_5)_6]^{3-}$ complex ion.

(a) Both assertion and reason are correct and reason is the correct explanation of assertion.

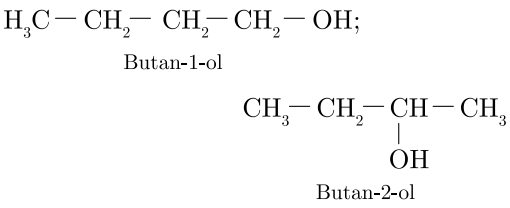
NODIA

58. Draw a pair of isomers for $C_4H_{10}O$ and name the type of isomerism.

ISC 2011

Ans :

The two isomers of $C_4H_{10}O$ are



Butan-1-ol

Butan-2-ol

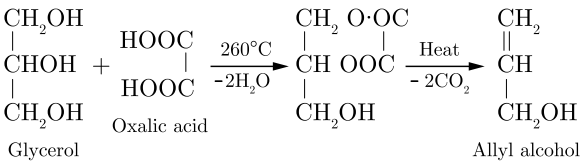
These two isomers have the same molecular formula, i.e. $C_4H_{10}O$ but they differ in the position of — OH group. Thus, the two compounds are showing position isomerism.

59. Write chemical equation for the given reaction and name the main product. Oxalic acid with glycerol at 260°C.

ISC 2005

Ans :

When glycerol is heated with oxalic acid at 260°C, glyceryl dioxalate is formed. It decomposes at once into CO_2 and allyl alcohol.



Glycerol Oxalic acid Allyl alcohol

60. Glycerol (propane-1, 2, 3-triol) is more viscous than ethylene glycol (ethane-1, 2-diol). Explain.

ISC 2016

Ans :

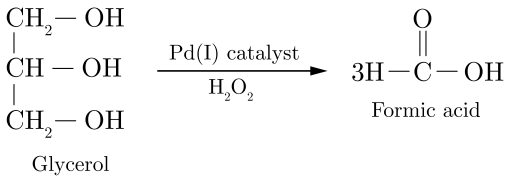
Glycerol (propane-1, 2, 3-triol) has three — OH groups per molecules, while ethylene glycol (ethane-1, 2-diol) has two — OH groups. The viscosity depends on the amount of hydrogen bonding between molecules and the more number of — OH bonds. There is greater hydrogen bonding in glycerol than ethylene glycol. So, glycerol is more viscous than ethylene glycol.

61. How can the following conversions be brought about?

Glycerol to formic acid

ISC 2015

Ans :



Glycerol Formic acid

NODIA

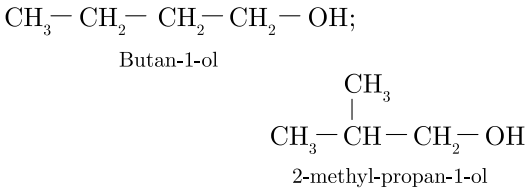
62. Name the type of isomerism exhibited by the following pairs of compounds.

1-butanol and 2-methyl-l-propanol

ISC 2013

Ans :

The given two compounds will show chain isomerism. The structural formula of the two compounds are



Butan-1-ol

2-methyl-propan-1-ol

The two compounds have the same molecular formula but different number of carbon atoms present in their parent chain.

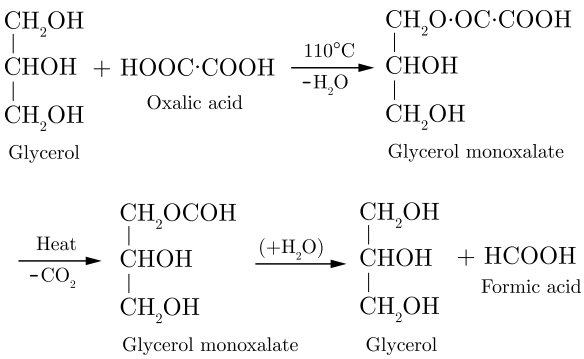
63. Give balanced equation for the following.

Glycerol is heated with oxalic acid at 110°C (383 K).

ISC 2011

Ans :

When glycerol is heated with crystalline oxalic acid at 110°C, it yields glycerol mono-formate which on hydrolysis gives glycerol and formic acid.



Glycerol Oxalic acid Glycerol monoxalate

Glycerol monoxalate Glycerol Formic acid

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79. Identify the compounds A and B in the given reaction.

ISC 2020

$$C_2H_5OH \xrightarrow[\Delta]{Cu} A \xrightarrow{\text{Dil. NaOH}} B$$

Ans :

$$x C_2H_5OH \xrightarrow[\Delta]{Cu} \underset{(A)}{CH_3CHO} \xrightarrow{\text{Dil.NaOH}} CH_3-\underset{\underset{CH_2CHO}{|}}{\overset{\overset{OH}{|}}{CH}} \quad (B)$$

80. Name the two organic compounds which have the same molecular formula C_2H_6O. Will they react with PCl_5? If they react, what are the products formed?

ISC 2025

Ans :

Ethanol (CH_3CH_2OH) and dimethyl ether (CH_3-O-CH_3) have the same molecular formula,

i.e. C_2H_6O.

Yes, only CH_3CH_2OH react with PCl_5.

$$CH_3CH_2OH + PCl_5 \longrightarrow CH_3CH_2Cl + POCl_3 + HCl$$

81. Give balanced equations and explain what happen when glycerol reacts with conc. H_2SO_4 ?

ISC 2024

Ans :

When glycerol is heated with conc. H_2SO_4, it eliminates two molecules of water and form acrolein.

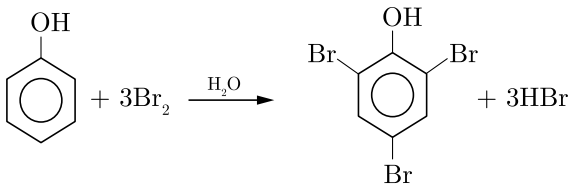
$$\underset{\text{Glycerol}}{\underset{\underset{CH_2OH}{|}}{\overset{\overset{CH_2-OH}{|}}{CH-OH}}{}} \xrightarrow[-2H_2O]{Conc.H_2SO_4} \underset{\text{(Unstable)}}{\underset{\underset{CHOH}{||}}{\overset{\overset{CH_2}{||}}{C}}{}} \xrightarrow{\text{Rearrangement}} \underset{\text{Acrolein}}{\underset{\underset{CHO}{|}}{\overset{\overset{CH_2}{||}}{CH}}{}}$$

82. Give balanced equation and explain what happens when phenol is treated with bromine water?

ISC 2000

Ans :

Reaction of phenol with bromine water produces white ppt. of 2, 4, 6-tribromophenol.



2,4,6-tribromophenol

83. How can the following conversion be brought about?

Propan-2-ol to acetoxime

ISC 2010

Ans :

Conversion of propan-2-ol into acetoxime.

$$\underset{\text{Propan-2-ol}}{CH_3-\underset{\underset{OH}{|}}{CH}-CH_3} \xrightarrow[K_2Cr_2O_7]{[O]} CH_3-\overset{\overset{O}{||}}{C}-CH_3 \xrightarrow{NH_2OH}$$

$$\underset{\text{Acetoxime}}{CH_3-\overset{\overset{CH_3}{|}}{C}=NOH} + H_2O$$

84. Complete the following reactions.

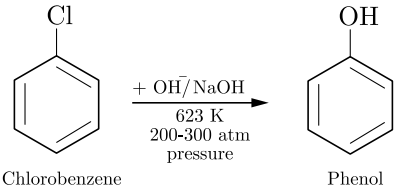
(i) Chlorobenzene to phenol

(ii) Diethyl ether to ethanol

ISC 2015

Ans :

(i) Conversion of chlorobenzene to phenol



Chlorobenzene Phenol

(ii) Conversion of diethyl ether to ethanol

$$\underset{\text{Diethyl ether}}{C_2H_5-O-C_2H_5} + HI \xrightarrow{\Delta} \underset{\text{Ethanol}}{C_2H_5OH} + C_2H_5I$$

85. Write the chemical equation for the dehydration of ethanol of with conc. H_2SO_4 at 140° and 170°C.

ISC Specimen 2023

Ans :

Ethanol can be dehydrated to give ethene by heating it with an excess of concentrated H_2SO_4 at 170°C.

$$\underset{\text{Ethanol}}{C_2H_5OH} + \underset{\text{Sulphuric acid}}{Conc.H_2SO_4} \xrightarrow{170^\circ C} \underset{\text{Ethene}}{C_2H_4} + H_2O$$

At 140°C, ethanol on reacting with conc. H_2SO_4 gives diethyl ether.

$$2C_2H_5OH \xrightarrow{\text{Conc. at } 140^\circ C(411K)} C_2H_5-O-C_2H_5 + H_3O$$

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TWO MARKS QUESTIONS

70. How is iodoform prepared from ethanol? Give the balanced equation.

ISC 2015

Ans :

$$CH_3 - CH_2 - OH + 4I_2 + 6NaOH \xrightarrow{\Delta} \underset{\text{Iodoform}}{CHI_3 \downarrow} + HCOO^{-}Na^{+} + 5NaI + 5H_2O$$

71. Give balanced chemical equations when ethyl alcohol is treated with thionyl chloride.

ISC 2020

Ans :

Ethyl alcohol is treated with thionyl chloride -

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH} + SOCl_2 \rightarrow \underset{\text{Ethyl chloride}}{C_2H_5Cl} + SO_2 + HCl$$

(Reaction with thionyl chloride).

72. Explain what happens when ethanol is heated with acetic acid in presence of conc. H_2SO_4?

ISC 2000

Ans :

When ethanol is heated with acetic acid in presence of conc. sulphuric acid, it forms ester.

$$\underset{\text{Ethanol}}{C_2H_5OH} + \underset{\text{Acetic acid}}{HOOC \cdot CH_3} \xrightarrow[\Delta]{\text{Conc. } H_2SO_4} \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + H_2O$$

73. Give one chemical test to distinguish between the following pairs of compounds.

Acetone and phenol

ISC 2021

Ans :

Phenol gives violet colour with neutral $FeCl_3$ solution while acetone does not give this test.

$$C_6H_5OH + FeCl_3 \longrightarrow \text{Violet colour}$$

$$CH_3COCH_3 + FeCl_3 \longrightarrow \text{No reaction}$$

74. Give one good chemical test to distinguish between the following pair of compounds.

Propan-1-ol and propan-2-ol

ISC 2010

Ans :

$$x C_2H_5OH \xrightarrow[\Delta]{Cu} \underset{(A)}{CH_3CHO} \xrightarrow{\text{Dil.NaOH}} CH_3-\underset{\underset{CH_2CHO}{|}}{\overset{\overset{OH}{|}}{CH}}$$

(B)

75. How will you bring about the following conversion?

Diethyl ether to ethanol

ISC 2008

Ans :

Diethyl ether $(C_2H_5 - O - C_2H_5)$ can be converted into ethanol by boiling it with water under pressure.

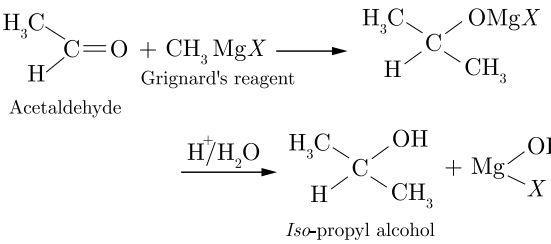
$$\underset{\text{Diethyl ether}}{C_2H_5 - O - C_2H_5} + HOH \xrightarrow{\text{Boiling}} \underset{\text{Ethanol}}{2C_2H_5OH}$$

76. How will you convert acetaldehyde to *iso*-propyl alcohol?

ISC 2002, 2000

Ans :

First of all acetaldehyde reacts with Grignard's reagent to form an addition product, which on hydrolysis gives *iso*-propyl alcohol.



77. Give one test to distinguish between phenol and benzoic acid.

ISC 2004

Ans :

$FeCl_3$ test Phenol gives violet colour with neutral $FeCl_3$ solution while benzoic acid gives buff coloured ppt.

$$3C_6H_5OH + FeCl_3 \longrightarrow \underset{\text{(Violet colour)}}{[(C_6H_5O)_3Fe]^{3-}} + 3HCl$$

$$3C_6H_5COOH + FeCl_3 \longrightarrow \underset{\text{(Buff coloured ppt.)}}{Fe(C_6H_5COO)_3} + 3HCl$$

78. Write chemical equation to illustrate the following name reaction.

Esterification reaction

ISC 2020, 2016

Ans :

Esterification is the reaction of an acid (condensation of the carboxyl group of the acid) with an alcohol (the hydroxyl group of the alcohol) in the presence of a catalyst.

$$\underset{\text{A carboxylic acid}}{R - \overset{\overset{O}{||}}{C} - OH} + \underset{\text{An alcohol}}{ROH} \overset{H^+}{\rightleftharpoons} \underset{\text{An ester}}{R - \overset{\overset{O}{||}}{C} - OR} + \underset{\text{Water}}{H_2O}$$

NODIA

ONE MARK QUESTIONS

49. Give the name of the following reaction.

ISC 2009

$$C_2H_5Br + C_2H_5ONa \longrightarrow C_2H_5OC_2H_5 + NaBr$$

Ans :

The given reaction is Williamson's synthesis used for the preparation of ether.

50. Give the balanced equation for the following reaction. Sodium ethoxide is treated with ethyl bromide.

ISC 2014

Ans :

$$\underset{\text{Sodium ethoxide}}{C_2H_5\overset{-}{O}\overset{+}{Na}} + \underset{\text{Ethyl bromide}}{C_2H_5Br} \longrightarrow \underset{\text{Diethyl ether}}{C_2H_5OC_2H_5} + NaBr$$

51. Give the chemical equation for the following.

Williamson's synthesis

ISC 2015

Ans :

In this method, alkyl halide is treated with a suitable sodium (or potassium) alkoxide.

$$\underset{\text{Sodium alkoxide}}{R-O^-Na^+} + \underset{\text{Alkyl halide}}{R'X} \longrightarrow \underset{\text{Ether}}{R-O-R'} + NaX$$

52. Give the balanced equation for the following reaction.

Chlorine is passed through diethyl ether.

ISC 2024

Ans :

With Cl_2, substitution takes place at α-C atom.

$$\underset{\text{Diethyl ether}}{CH_3CH_2-O-CH_2CH_3} \xrightarrow[-HCl]{+Cl_2} \underset{\alpha-\text{chlorodiethyl ether}}{CH_3CHClOCH_2CH_3}$$

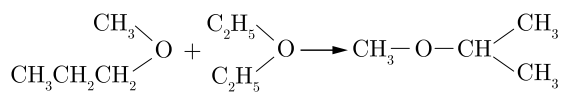
$$\xrightarrow[-HCl]{+Cl_2} \underset{\alpha,\alpha'-\text{dichlorodiethyl ether}}{CH_3CHCl \cdot OCHClCH_3}$$

53. Write the structures of the isomeric ethers with the formula $C_4H_{10}O$.

ISC 2001

Ans :

Isomeric ethers with formula $C_4H_{10}O$ are as



Methyl proply ether Diethyl ether Methyl *iso*-proply ether

54. Why do alcohols possess higher boiling points as compared to those of corresponding alkanes?

ISC 2017

Ans :

Due to the presence of strong hydrogen bonding between alcohol molecules, they possess higher boiling point as compared to their corresponding alkanes.

55. How will you obtain the following? (Give balanced chemical equations)

ISC 2019

Propan -2- of from Grignard's reagent

Ans :

$$CH_3CHO \xrightarrow[(ii)\ H_2O/H^+]{(i)\ CH_3MgX} \underset{\text{Propan-2-ol}}{CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}HOH} + Mg(OH)$$

56. How can the following conversions be brought about? Acetaldehyde to propan-2-ol

ISC 2017

Ans :

$$\underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{CH_3MgBr} \underset{\text{Addition product}}{\left[CH_3-\overset{\displaystyle OMgBr}{\overset{\displaystyle |}{C}}H-CH_3\right]} \xrightarrow[-Mg(OH)Br]{H^+/H_2O} \underset{\text{Propan-2-ol}}{CH_3-\overset{\displaystyle OH}{\overset{\displaystyle |}{C}}H-CH_3}$$

57. Give balanced equation for the following reaction.

1-butanol and hydrogen chloride

ISC 2012

Ans :

Alcohol (butan-l-ol) reacts with hydrogen chloride to form chloroalkane (chlorobutane).

$$\underset{\text{Butan-1-ol}}{CH_3-CH_2-CH_2-CH_2-OH} + HCl \xrightarrow{\text{Anhyd. } ZnCl_2} \underset{\text{Chlorobutane}}{CH_3-CH_2-CH_2-CH_2-Cl} + H_2O$$

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At 110°C, ethanol on reacting with conc. H_2SO_4 gives ethyl hydrogen sulphate

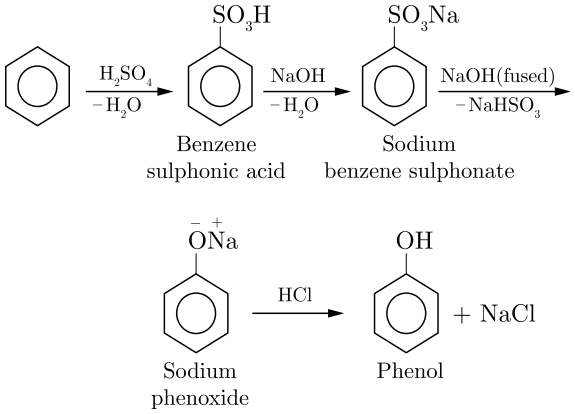
$$CH_3CH_2OH \xrightarrow[110^\circ C]{Conc.H_2SO_4} CH_3CH_2OSO_3H$$

86. How can you convert benzene to phenol?

ISC 2012

Ans :

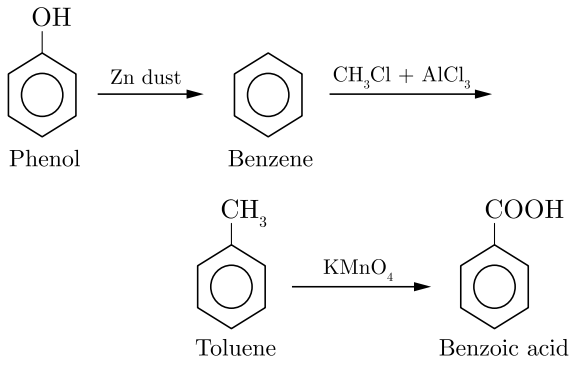
Conversion of benzene to phenol is as follows



87. How is phenol converted to benzoic acid? Explain with the help of balanced chemical equations.

ISC Specimen 2018

Ans :



88. Give one chemical test to distinguish between the following pair of compound.

Propan-1-ol and propan-2-ol

ISC 2020

Ans :

Propan-1-ol and propan-2-ol can be distinguished by Lucas test. When Lucas reagent (solution of HCl and $ZnCl_2$) is added to propan-2-ol, cloudiness (turbidity) appears within 5 min. When Lucas reagent is added to propan-1-ol, no turbidity appears at room temperature and solution remains clear.

$$\underset{\text{Propan-1-ol}}{CH_3CH_2CH_2-OH} \xrightarrow[ZnCl_2]{\text{Conc. HCl}} \text{No turbidity appears at room temperature}$$

$$\underset{\text{Propan-2-ol}}{CH_3-\underset{\underset{OH}{|}}{CH}-CH_3} \xrightarrow[ZnCl_2]{\text{Conc. HCl}} \text{Turbidity appears within 5 minutes}$$

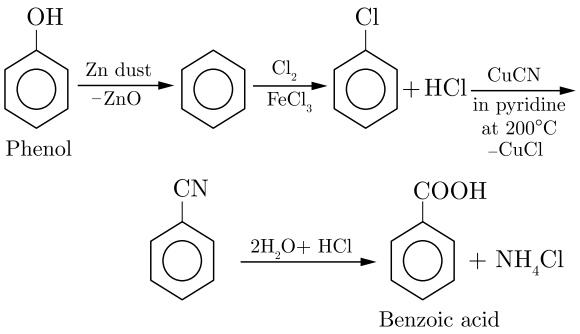
89. How will you bring about the following conversion?

Phenol to benzoic acid

ISC 2009

Ans :

Conversion of phenol to benzoic acid is as follows

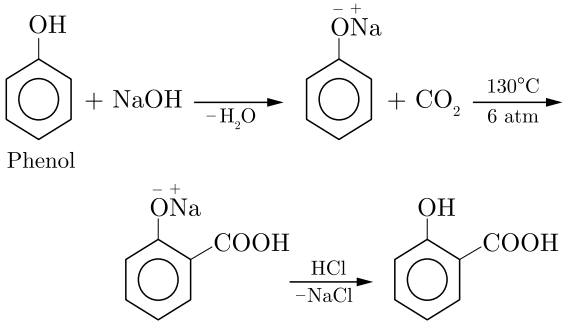


90. How will you convert phenol to salicylic acid?

ISC 2004

Ans :

Conversion of phenol to salicylic acid is as follows



This reaction is named as Kolbe's reaction.

91. Give reason why phenol is more easily nitrated than benzene?

ISC 2001

Ans :

In phenol, −OH group activates the benzene ring and increases the electron density at *ortho* and *para*-positions. Hence, nitration (an electrophilic substitution) can be carried out easily.

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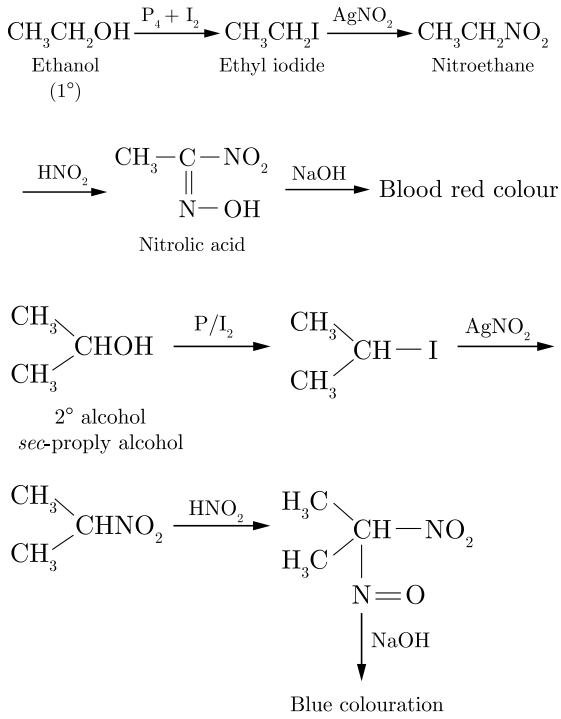


100. How will you obtain the following? (Give balanced chemical equations)

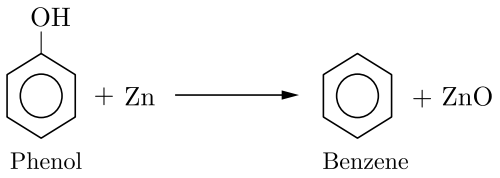
ISC 2021

(i) Benzene from phenol

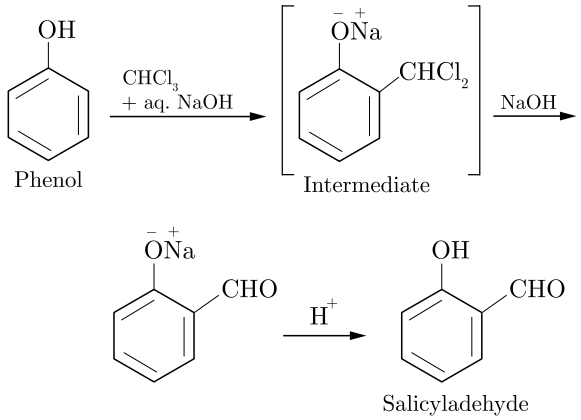
(ii) Salicylaldehyde from phenol

Ans :

(i) Reaction involve for the formation of benzene from phenol is as follows



(ii) Reaction involve for the formation of salicylaldehyde from phenol is as follows



THREE MARKS QUESTIONS

101. Explain why phenol is soluble in sodium hydroxide solution whereas ethanol is not.

ISC 2000

Ans :

Phenol is acidic enough to react with sodium hydroxide forming sodium phenoxide.

$C_6H_5OH + NaOH \rightarrow C_6H_5ONa + H_2O$

Phenoxide ion formed is stabilised by resonance.

Ethanol is much less acidic and cannot react with sodium hydroxide effectively.

Therefore ethanol does not dissolve in sodium hydroxide solution.

102. Explain the acidic character of alcohols on the basis of their reaction with Grignard reagents.

ISC 2021

Ans :

Alcohols react with Grignard reagents because they contain acidic hydrogen atom in hydroxyl group.

$ROH + RMgX \rightarrow RH + Mg(OR)X$

The Grignard reagent abstracts proton from alcohol producing hydrocarbon.

This reaction demonstrates weak acidic nature of alcohols.

Therefore Grignard reagents must be used under strictly anhydrous conditions.

103. Write the names and structures of three isomers which have the same molecular formula C_3H_8O.

ISC 2008

Ans :

Three isomers which have the same molecular formula C_3H_8O are as follows.

(i) $\underset{\text{Propan-1-ol}}{CH_3-CH_2-CH_2-OH}$

(ii) $CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$

Propan-2-ol

(iii) $\underset{\text{Methoxyethane}}{CH_3-CH_2-O-CH_3}$

Structures (i) and (ii) are the position isomers.

Structures (ii) and (iii) or structures (i) and (iii) are the functional isomers of each other.

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96. Carry out the following conversion :
Ethanol to acetone

ISC 2011

Ans :

The reactions involved to convert ethanol into acetone are as follows

$$\underset{\text{Ethanol}}{CH_3CH_2OH} + O_2 \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \underset{\text{Acetaldehyde}}{CH_3CHO} + H_2O$$

$$\underset{\text{Ethanol}}{2CH_3CHO} + CH_3MgBr \longrightarrow CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-\overset{-}{O}\overset{+}{M}gBr$$

Additive product

$$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-\overset{-}{O}\overset{+}{M}gBr + H_2O \xrightarrow{\text{Hydrolysis}}$$

$$\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\diagdown}}CHOH \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\diagdown}}C=O + H_2O$$

Acetone

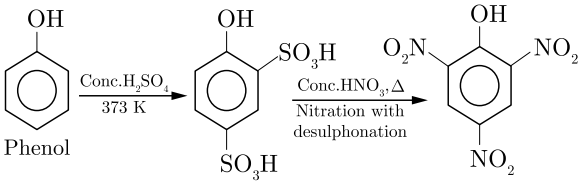
97. How will you obtain the following? (Give balanced equation)

ISC 2024

(i) Picric acid from phenol
(ii) Anisole form phenol

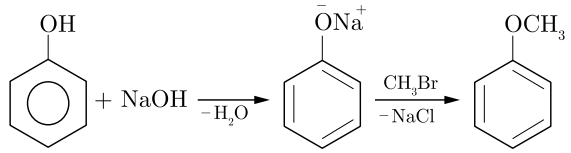
Ans :

(i) Picric acid from phenol Phenol is treated with conc. HNO_3 and conc. H_2SO_4 to yield 2, 4, 6-trinitrophenol (picric acid).



Phenol — Phenol-2,4-disulphonic acid — Picric acid

(ii) Anisole from phenol Phenol reacts with aqueous NaOH to form sodium phenoxide which on reaction with methyl bromide forms anisole.



Phenol — Sodium phenoxide — Anisole

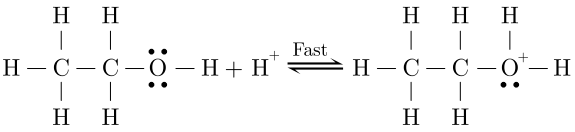
98. Write the mechanism of acid dehydration of ethanol to yield ethene.

ISC 2018

Ans :

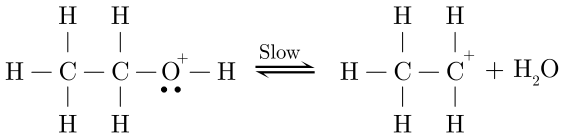
The mechanism of dehydration of ethanol involves the following steps

Step I : Formation of protonated alcohol

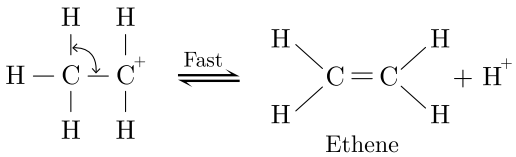


Ethanol — Protonated alcohol (Ethyl oxonium ion)

Step II : Formation of carbocation It is the slowest step and hence, the rate determining step of the reaction.



Step III : Formation of ethene by the elemination of a proton



Ethanol — Ethene

99. Give chemical test to distinguish:
Ethyl alcohol and *sec*-propyl alcohol.

ISC 2017

Ans :

Ethanol is primary alcohol while propan-2-ol is secondary alcohol. So, the two can be distinguished by Victor Meyer's test.

The reactions involved for the two alcohols are as follows

NODIA

Hence primary alkyl halides are preferred for successful ether synthesis.

133. A student oxidised ethanol, propan-2-ol and tert-butyl alcohol separately using acidified potassium dichromate solution. Different observations were obtained for the three alcohols. The teacher explained that oxidation behaviour depends upon the type of alcohol and the presence of hydrogen atom on the carbon attached to hydroxyl group.
(i) Which alcohol forms a ketone on oxidation?
(ii) Which alcohol resists oxidation under ordinary conditions?
(iii) Explain why tertiary alcohols resist oxidation.

Ans :
(i) Propan-2-ol.
(ii) Tert-butyl alcohol.
(iii) Oxidation of alcohols requires removal of hydrogen atom from the carbon attached to hydroxyl group. Tertiary alcohols do not contain such hydrogen atoms. Therefore oxidation becomes difficult without breaking carbon-carbon bonds and tertiary alcohols resist oxidation under ordinary conditions.

134. A chemist treated phenol with bromine water and immediately obtained a white precipitate without using any catalyst. The reaction occurred much faster than bromination of benzene. The teacher explained that the hydroxyl group strongly influences the reactivity of benzene ring.
(i) Name the white precipitate formed during the reaction.
(ii) At which positions does bromination mainly occur in phenol?
(iii) Explain why phenol undergoes bromination more readily than benzene.

Ans :
(i) 2,4,6-Tribromophenol.
(ii) Ortho and para positions.
(iii) The hydroxyl group donates electron density to the benzene ring through resonance effect increasing electron density particularly at ortho and para positions. Therefore electrophilic substitution occurs readily in phenol even without catalyst whereas benzene requires Lewis acid catalyst.

135. A student carried out Reimer-Tiemann reaction using phenol, chloroform and aqueous sodium hydroxide. The major product obtained contained both hydroxyl and aldehyde functional groups attached to the benzene ring.
(i) Name the major product formed in the reaction.
(ii) Which reactive intermediate is generated from chloroform?
(iii) Explain the role of aqueous sodium hydroxide in the reaction.

Ans :
(i) Salicylaldehyde.
(ii) Dichlorocarbene.
(iii) Aqueous sodium hydroxide converts chloroform into dichlorocarbene intermediate. It also converts phenol into phenoxide ion which activates the aromatic ring towards electrophilic attack. Consequently formyl group enters mainly at ortho position producing salicylaldehyde after hydrolysis.

136. A chemistry student performed Lucas test on three alcohol samples. One sample produced immediate turbidity, another showed turbidity after a few minutes and the third showed no turbidity at room temperature.
(i) Which type of alcohol gives immediate turbidity?
(ii) Which alcohol reacts slowest with Lucas reagent?
(iii) Explain the basis of Lucas test.

Ans :
(i) Tertiary alcohol.
(ii) Primary alcohol.
(iii) Lucas test is based on differences in reactivity of alcohols towards concentrated HCl in presence of anhydrous $ZnCl_2$. Tertiary alcohols form stable carbocations rapidly producing insoluble alkyl chlorides immediately. Secondary alcohols react slowly while primary alcohols react only on heating because carbocation formation is difficult.

137. An industrial chemist explained that phenol and acetone are commercially prepared from cumene. The process involves oxidation followed by acidic cleavage of an intermediate compound. Both products obtained are industrially very important.
(i) Name the industrial process used for preparation of phenol from cumene.
(ii) Name the intermediate formed during oxidation of cumene.
(iii) Explain why this process is economically important.

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104. A student added neutral $FeCl_3$ solution separately to ethanol and phenol. Only one compound produced a violet coloured solution. Identify the compound and explain the observation.

ISC 2024

Ans :

Phenol produces violet coloured solution with neutral $FeCl_3$.

Phenol reacts with ferric chloride forming ferric phenoxide complex.

The coloured complex is formed due to interaction between phenoxide ion and ferric ion.

Alcohols do not form such complexes and therefore ethanol does not give the characteristic violet colouration.

105. During dehydration reactions, ethanol forms different products at 413 K and 443 K in presence of concentrated H_2SO_4. Explain the products formed under both conditions.

ISC 2021

Ans :

At 413 K, intermolecular dehydration of ethanol occurs forming diethyl ether.

$$2C_2H_5OH \xrightarrow{\text{conc.}H_2SO_4,\ 413K} C_2H_5OC_2H_5 + H_2O$$

At 443 K, intramolecular dehydration takes place producing ethene.

$$C_2H_5OH \xrightarrow{\text{conc.}H_2SO_4,\ 443K} CH_2 = CH_2 + H_2O$$

Higher temperature favours elimination reaction and alkene formation.

106. A chemist attempted oxidation of three alcohols: ethanol, propan-2-ol and tert-butyl alcohol. Only one alcohol resisted oxidation under ordinary conditions. Identify the alcohol and justify your answer.

ISC 2025

Ans :

Tert-butyl alcohol resists oxidation under ordinary conditions.

Oxidation of alcohols requires presence of hydrogen atom on the carbon attached to hydroxyl group.

Tertiary alcohols do not possess such hydrogen atoms.

Therefore oxidation becomes difficult without cleavage of carbon-carbon bonds and tertiary alcohols resist oxidation.

107. Explain why phenol undergoes bromination readily without catalyst whereas benzene requires Lewis acid catalyst for bromination.

ISC 2014

Ans :

In phenol, the hydroxyl group donates electron density to the benzene ring through resonance effect.

This increases electron density particularly at ortho and para positions making the ring highly reactive towards electrophiles.

Therefore bromination occurs readily without catalyst.

Benzene lacks activating groups and hence requires Lewis acid catalyst such as $FeBr_3$.

108. A student prepared methoxyethane using sodium methoxide and bromoethane. Name the reaction involved and explain why primary alkyl halides are preferred in this method.

ISC 2011

Ans :

The reaction involved is Williamson ether synthesis.

$$CH_3ONa + C_2H_5Br \rightarrow CH_3OC_2H_5 + NaBr$$

Primary alkyl halides are preferred because they undergo nucleophilic substitution easily due to low steric hindrance.

Tertiary alkyl halides mainly undergo elimination reactions instead of ether formation.

109. A student treated phenol with chloroform and aqueous sodium hydroxide and obtained a compound having aldehyde group attached to the benzene ring. Name the reaction and explain the role of chloroform in the reaction.

ISC 2024

Ans :

The reaction is Reimer-Tiemann reaction.

Chloroform reacts with aqueous sodium hydroxide forming dichlorocarbene intermediate.

The electrophile attacks the activated phenol ring mainly at ortho position.

Subsequent hydrolysis introduces formyl group producing salicylaldehyde as the major product.

110. Explain why alcohols have higher boiling points than hydrocarbons of comparable molecular masses.

ISC 2002

Ans :

Alcohol molecules contain hydroxyl groups capable of forming strong intermolecular hydrogen bonds.

These intermolecular attractions require large amount of energy to break during boiling.

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Hydrocarbons are non-polar and possess only weak van der Waals forces.

Therefore alcohols possess much higher boiling points.

123. Explain why phenol undergoes bromination readily without catalyst whereas benzene requires catalyst.

ISC 2024

Ans :

The hydroxyl group attached to benzene ring donates electron density through resonance effect.

This increases electron density especially at ortho and para positions.

Consequently electrophilic substitution occurs readily even without catalyst.

$C_6H_5OH + 3Br_2 \rightarrow C_6H_2Br_3OH + 3HBr$

Benzene lacks activating groups and therefore requires Lewis acid catalyst such as $FeBr_3$.

124. Explain Lucas test for distinguishing primary, secondary and tertiary alcohols.

ISC 2000

Ans :

Lucas reagent contains concentrated HCl and anhydrous $ZnCl_2$.

Tertiary alcohols react immediately producing turbidity due to rapid formation of insoluble alkyl chlorides.

Secondary alcohols produce turbidity after few minutes.

Primary alcohols do not show turbidity at room temperature because carbocation formation is difficult.

Thus Lucas test distinguishes different classes of alcohols.

125. Explain why phenol is more reactive than benzene towards electrophilic substitution reactions.

ISC 2021

Ans :

The hydroxyl group attached to benzene ring donates electron density through resonance effect.

Electron density increases particularly at ortho and para positions.

Therefore electrophiles attack the aromatic ring more readily.

Phenol undergoes nitration, bromination and sulphonation under mild conditions whereas benzene requires catalyst and harsher conditions for similar reactions.

126. Explain the action of hot reduced copper at 573 K on primary, secondary and tertiary alcohols.

ISC 2017

Ans :

Primary alcohols undergo dehydrogenation producing aldehydes.

$CH_3CH_2OH \xrightarrow{Cu,\ 573K} CH_3CHO + H_2$

Secondary alcohols form ketones.

$CH_3CHOHCH_3 \xrightarrow{Cu,\ 573K} CH_3COCH_3 + H_2$

Tertiary alcohols undergo dehydration producing alkenes because dehydrogenation is not possible due to absence of hydrogen on hydroxyl-bearing carbon atom.

127. Describe the preparation and important properties of phenol obtained by Cumene process.

ISC 2023

Ans :

In Cumene process, cumene undergoes oxidation forming cumene hydroperoxide which on acidic cleavage gives phenol and acetone.

Phenol obtained is weakly acidic and reacts with sodium hydroxide forming sodium phenoxide.

It undergoes electrophilic substitution reactions readily due to activating hydroxyl group.

The process is economically important because both phenol and acetone are valuable industrial chemicals.

CASE BASED QUESTIONS

128. A student compared the boiling points of ethanol and dimethyl ether having nearly the same molecular mass. He observed that ethanol possesses a much higher boiling point. The chemistry teacher explained that intermolecular forces play an important role in determining physical properties of organic compounds. The presence or absence of hydrogen bonding significantly affects boiling points.

(i) Which intermolecular force is mainly responsible for the high boiling point of ethanol?

(ii) Why is dimethyl ether unable to form strong intermolecular hydrogen bonding?

(iii) Explain why ethanol has a much higher boiling point than dimethyl ether.

NODIA

Ans :

At 413 K, intermolecular dehydration of ethanol occurs producing diethyl ether.

$$2C_2H_5OH \xrightarrow{\text{conc.}H_2SO_4,\ 413\ K} C_2H_5OC_2H_5 + H_2O$$

At 443 K, intramolecular dehydration takes place forming ethene.

$$C_2H_5OH \xrightarrow{\text{conc.}H_2SO_4,\ 443K} CH_2 = CH_2 + H_2O$$

Lower temperature favours ether formation while higher temperature favours elimination and alkene formation.

117. Explain why phenol is more acidic than ethanol. Give suitable reactions in support of your answer.

ISC 2010

Ans :

Phenol is more acidic because the phenoxide ion formed after loss of proton is resonance stabilised.

The negative charge gets delocalised over the aromatic ring.

$$C_6H_5OH + NaOH \rightarrow C_6H_5ONa + H_2O$$

Ethanol does not react with sodium hydroxide because ethoxide ion is not resonance stabilised.

Thus phenol releases proton more easily than ethanol and shows greater acidic character.

118. Describe Reimer-Tiemann reaction. Explain the role of chloroform in this reaction.

ISC 20114

Ans :

In Reimer-Tiemann reaction, phenol reacts with chloroform in presence of aqueous sodium hydroxide producing salicylaldehyde.

$$C_6H_5OH + CHCl_3 + 3NaOH \rightarrow o - HOC_6H_4CHO + 3NaCl + 2H_2O$$

Chloroform forms dichlorocarbene intermediate in alkaline medium.

The electrophile attacks activated phenol ring mainly at ortho position followed by hydrolysis to form salicylaldehyde.

119. Explain Williamson ether synthesis. Why are tertiary alkyl halides not suitable for this synthesis?

ISC 2024

Ans :

Williamson ether synthesis involves reaction of sodium alkoxide with alkyl halide.

$$C_2H_5ONa + CH_3Br \rightarrow CH_3OC_2H_5 + NaBr$$

The reaction proceeds through nucleophilic substitution mechanism.

Primary alkyl halides are preferred because steric hindrance is minimum.

Tertiary alkyl halides mainly undergo elimination reactions in presence of strong bases instead of substitution, therefore they are unsuitable for ether synthesis.

120. Explain the mechanism of acidic dehydration of ethanol to ethene.

ISC 2020

Ans :

Step 1 : Protonation of ethanol

$$C_2H_5OH + H^+ \rightarrow C_2H_5OH_2^+$$

Step 2 : Removal of water molecule producing carbocation intermediate.

$$C_2H_5OH_2^+ \rightarrow C_2H_5^+ + H_2O$$

Step 3 : Elimination of proton from carbocation producing ethene.

$$C_2H_5^+ \rightarrow CH_2 = CH_2 + H^+$$

Thus concentrated sulphuric acid acts as dehydrating agent converting alcohol into alkene.

121. Distinguish between alcohols and phenols on the basis of reactions with sodium hydroxide, neutral ferric chloride and bromine water.

ISC 2025

Ans :

Test	**Alcohols**	**Phenols**
Reaction with NaOH	No reaction	Forms sodium phenoxide
Neutral $FeCl_3$ test	No colour	Violet coloration
Bromine water	No reaction	White precipitate of 2,4,6-tribromophenol

These reactions help distinguish alcohols from phenols experimentally.

122. Explain why alcohols have higher boiling points than ethers and hydrocarbons having comparable molecular masses.

ISC 2010

Ans :

Alcohol molecules contain hydroxyl groups capable of forming strong intermolecular hydrogen bonds.

Considerable energy is required to break these interactions during boiling.

Ethers cannot form intermolecular hydrogen bonding effectively because they lack hydrogen attached directly to oxygen.

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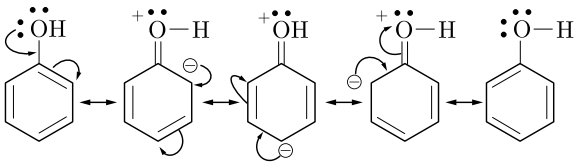


While in benzene, no such activating group is present, thus nitration is carried out under only in special conditions.

92. How will the following be obtained? (Give chemical equation)

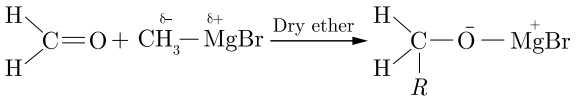
ISC 2023

(i) Ethanol form Grignard's reagent.

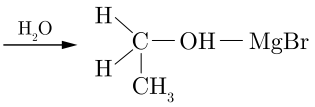
(ii) Diethyl ether form sodium ethoxide.

Ans :

(i) When methanal reacts with methyl magnesium bromide in the presence of dry ether to give a complex which on hydrolysis gives ethanol.



Adduct



Ethanol

(ii) Williamson's synthesis

$$\underset{\text{Sodium ethoxide}}{CH_3-CH_2-ONa} + \underset{\text{Ethyl bromide}}{Br-CH_2-CH_3} \xrightarrow{\Delta} \underset{\text{Diethyl ether}}{CH_3-CH_2-O-CH_2-CH_3} + NaBr$$

93. How will you obtain the following? (Give balanced equation)

(i) Ethyl chloride from diethyl ether

(ii) Ethyl acetate from ethanol

ISC 2018

Ans :

(i) Ethyl chloride from diethyl ether Diethyl ether reacts with phosphorus pentachloride to give ethyl chloride and phosphoryl chloride.

$$\underset{\text{Diethyl ether}}{C_2H_5-O-C_2H_5} + PCl_5 \longrightarrow \underset{\text{Ethyl chloride}}{2C_2H_5Cl} + POCl_3$$

(ii) Ethyl acetate from ethanol Ethyl acetate is an ester formed by reaction between ethanol and ethanoic acid. Ethanol is first oxidised to ethanoic acid, which further react with ethanol to form ethyl acetate

$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow{\text{Alkaline } KMnO_4} \underset{\text{Ethanoic acid}}{CH_3COOH}$$

$$CH_3COOH + CH_3CH_2OH \xrightarrow{\text{Conc. } H_2SO_4} \underset{\text{Ethyl acetate}}{CH_3COOCH_2CH_3} + H_2O$$

94. How will the following be obtained? (Give chemical equations)

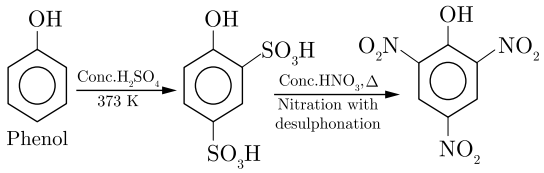
ISC Specimen 2023

(i) Picric acid from phenol

(ii) Ethanol from formaldehyde

Ans :

(i) Picric acid from phenol Phenol is treated with conc. HNO_3 and conc. H_2SO_4 to yield 2, 4, 6-trinitrophenol (picric acid).



Phenol-2,4-disulphonic acid

Picric acid

(ii) Formaldehyde is converted to ethanol by adding Grignard's reagent.

$$\underset{\text{Formaldehyde}}{HCHO} + CH_3MgBr \longrightarrow \underset{\text{Ethanol}}{CH_3CH_2OH}$$

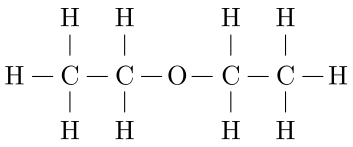
95. Write the structure of three ethers with molecular formula $C_4H_{10}O$.

ISC 2016

Ans :

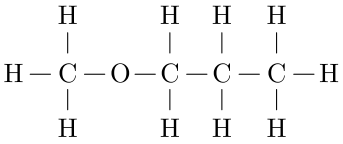
The three ethers with molecular formula $C_4H_{10}O$ are diethylether, methoxypropane and methyl *iso*-propyl ether.

(i)



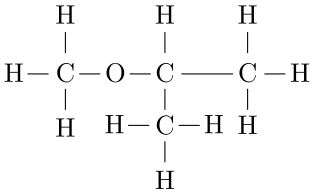
Diethyl ether

(ii)



Methoxy propane

(iii)



Methyl *iso*-propyl ether

NODIA

Ans :

(i) Intermolecular hydrogen bonding.

(ii) Dimethyl ether does not contain hydrogen atom directly attached to oxygen atom.

(iii) Ethanol molecules are associated through strong intermolecular hydrogen bonds due to the presence of hydroxyl group. Large amount of energy is therefore required to separate ethanol molecules during boiling. Dimethyl ether lacks such intermolecular hydrogen bonding and hence possesses lower boiling point.

129. A student treated ethanol with concentrated sulphuric acid under different temperature conditions. At 413 K, one product was obtained whereas at 443 K, an entirely different product was formed. The teacher explained that reaction conditions determine whether intermolecular or intramolecular dehydration occurs in alcohols.

(i) Which product is formed at 413 K?

(ii) Which product is formed at 443 K?

(iii) Explain why different products are formed at different temperatures.

Ans :

(i) Diethyl ether.

(ii) Ethene.

(iii) At lower temperature (413 K) intermolecular dehydration predominates producing ether. At higher temperature (443 K) elimination becomes more favourable and intramolecular dehydration occurs forming alkene. Thus temperature controls the reaction pathway and final product obtained from ethanol.

130. A chemist compared the acidic behaviour of ethanol and phenol using sodium hydroxide solution. Phenol dissolved readily whereas ethanol showed no reaction. The chemist explained that stability of conjugate base formed after loss of proton determines acidic strength of organic compounds.

(i) Which compound reacts with sodium hydroxide solution?

(ii) What is the product formed when phenol reacts with sodium hydroxide?

(iii) Explain why phenol is more acidic than ethanol.

Ans :

(i) Phenol.

(ii) Sodium phenoxide.

(iii) Phenol forms phenoxide ion after losing proton. The negative charge in phenoxide ion gets delocalised over the aromatic ring through resonance and becomes stabilised. Ethoxide ion formed from ethanol lacks resonance stabilisation. Therefore phenol releases proton more easily and behaves as a stronger acid.

131. A laboratory assistant added neutral ferric chloride solution separately to ethanol and phenol. Only one compound produced a violet coloured solution. The teacher explained that this reaction is commonly used as a qualitative test in organic chemistry.

(i) Which compound gives violet coloration with neutral $FeCl_3$ solution?

(ii) Name the coloured complex formed during the reaction.

(iii) Explain why ethanol does not produce similar colouration.

Ans :

(i) Phenol.

(ii) Ferric phenoxide complex.

(iii) Phenol forms phenoxide ion which reacts with ferric ions producing coloured complex. Ethanol lacks phenolic hydroxyl group and cannot form similar resonance stabilised complex with ferric chloride. Therefore ethanol does not give violet coloration with neutral ferric chloride solution.

132. A student prepared methoxyethane in the laboratory by reacting sodium methoxide with bromoethane. The chemistry teacher explained that the reaction proceeds through nucleophilic substitution and is widely used for ether preparation.

(i) Name the reaction used for preparation of ether.

(ii) Which reagent acts as nucleophile in this reaction?

(iii) Why are primary alkyl halides preferred in this synthesis?

Ans :

(i) Williamson ether synthesis.

(ii) Sodium methoxide.

(iii) Primary alkyl halides possess minimum steric hindrance and therefore undergo nucleophilic substitution reactions readily. Tertiary alkyl halides mainly undergo elimination reactions in presence of strong bases such as alkoxides.

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Hydrocarbons cannot form hydrogen bonds because they are non-polar molecules.

Therefore alcohols possess significantly higher boiling points than hydrocarbons of similar molecular masses.

111. A student observed that phenol reacts readily with dilute nitric acid whereas benzene does not. Explain the reason and name the major product formed.

ISC 2010

Ans :

The hydroxyl group in phenol activates the benzene ring by donating electron density through resonance.

Therefore electrophilic substitution reactions occur readily in phenol under mild conditions.

Phenol reacts with dilute nitric acid mainly producing o-nitrophenol and p-nitrophenol.

Benzene lacks activating groups and therefore reacts much more slowly.

112. According for the following.

ISC 2023

(i) Phenol is a stronger acid than aliphatic alcohols.

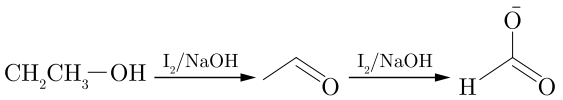
(ii) Ethanol gives iodoform reaction whereas methanol does not give iodoform reaction.

(iii) Ethers should not be distilled to dryness.

Ans :

(i) Phenol is a stronger acid due to the presence of polar $-OH$ group and resonance stabilisation of phenoxide ion. This resonance stabilisation of phenoxide ion makes phenol more acidic than aliphatic alcohols.

(ii) Compounds that can be oxidised to methyl ketone or having methyl group attached to carbonyl carbon can gave haloform reaction. Thus, ethyl alcohol (ethanol) can be oxidised to ethanal which contains methyl keto group but methyl alcohols do not, as it cannot oxidised to methyl keto group.



Ethanol Iodoform

(iii) Ethers are not distilled to dryness for the fear of explosion due to formation of peroxides. Peroxides are highly explosive and are less volatile than ethers.

FOUR MARKS QUESTIONS

113. Describe Kolbe's reaction with suitable equations. Mention its importance.

ISC 2004

Ans :

In Kolbe's reaction, sodium phenoxide reacts with carbon dioxide under pressure forming sodium salicylate.

$$C_6H_5ONa + CO_2 \xrightarrow{\text{pressure}} o - HOC_6H_4COONa$$

On acidification:

$$o - HOC_6H_4COONa + HCl \rightarrow o - HOC_6H_4COOH + NaCl$$

Salicylic acid obtained is used in preparation of aspirin and medicinal compounds.

114. Explain the preparation of alcohols from Grignard reagents with suitable example.

ISC 2014

Ans :

Grignard reagents react with carbonyl compounds forming magnesium alkoxides which on hydrolysis produce alcohols.

Example :

$$CH_3MgBr + HCHO \rightarrow CH_3CH_2OMgBr$$

$$CH_3CH_2OMgBr + H_2O \rightarrow CH_3CH_2OH + Mg(OH)Br$$

The reaction is important for preparation of primary, secondary and tertiary alcohols depending upon carbonyl compound used.

115. Explain oxidation reactions of primary, secondary and tertiary alcohols with suitable equations.

ISC 2003

Ans :

Primary alcohols oxidise to aldehydes and further to carboxylic acids.

$$CH_3CH_2OH \xrightarrow{[O]} CH_3CHO \xrightarrow{[O]} CH_3COOH$$

Secondary alcohols oxidise to ketones.

$$CH_3CHOHCH_3 \xrightarrow{[O]} CH_3COCH_3$$

Tertiary alcohols resist oxidation because they lack hydrogen atom on carbon attached to hydroxyl group.

116. A student treated ethanol separately with concentrated H_2SO_4 at 413 K and 443 K. Different products were obtained under the two conditions. Explain the reactions involved with suitable equations.

ISC 2023

NODIA

Ans :

(i) Cumene process.

(ii) Cumene hydroperoxide.

(iii) The process simultaneously produces two valuable industrial chemicals, phenol and acetone. Phenol is widely used in manufacture of plastics, drugs and dyes while acetone is an important industrial solvent. Therefore the process is economically advantageous and extensively used on commercial scale.

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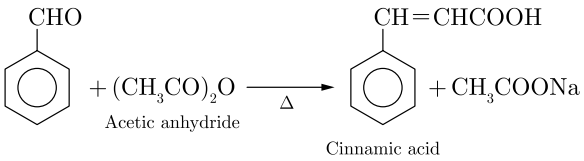
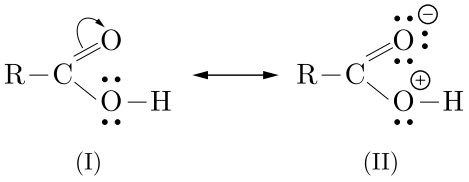
Parkin's reaction (Name Reaction) :



Structure of carboxylic acids :

Carboxylic acids are the compounds having the carboxyl functional group (–COOH).

The carbonyl carbon involves sp^2 hybridisation leaving one hydrbridised p orbital. This p orbital can overlap sidewise with either of the p orbital of oxygen atom forming π-bonds. The resulting π electron cloud is spread over both oxygen and carbon atom. This delocalisation gives the stability to the carboxylate ion. Monocarboxylic acid has two resonating structures.



General Methods of preparation of carboxylic acids :

(i) **From oxidation of primary alcohols :**

$$RCH_2OH \xrightarrow[KMnO_4/Dil.H_2SO_4]{[O]} RCHO \xrightarrow[KMnO_4/Dil.H_2SO_4]{[O]} RCOOH$$

(ii) **From oxidation of aldehydes and ketones :**

$$RCHO \xrightarrow[KMnO_4/KOH]{[O]} RCOOH$$

(iii) **From hydrolysis of cyanides :**

$$R-CN \xrightarrow[H^+]{\text{hydrolysis}} RCOOH$$

(iv) **From grignard reagent :**

$$CH_3MgBr + CO_2 \xrightarrow{\text{Dry ether}} O=C(CH_3)-OMgBr \xrightarrow[H^+]{H_2O} CH_3COOH + Mg(OH)Br$$

(v) **By hydrolysis of esters :**

$$RCOOR' + H_2O \xrightarrow{H^+} RCOOH + R'OH$$

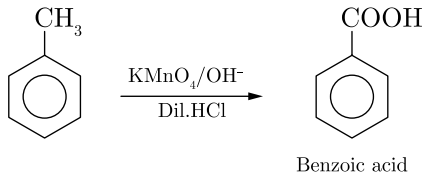
(vi) **From alkenes :**

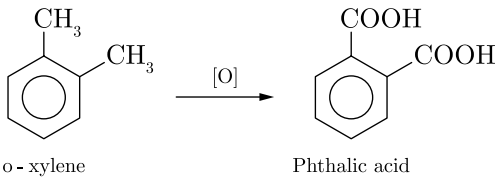
$$CH_2=CH_2 + CO + H_2O \xrightarrow[\Delta]{H_3PO_4} \underset{\text{Propanoic acid}}{CH_3CH_2COOH}$$

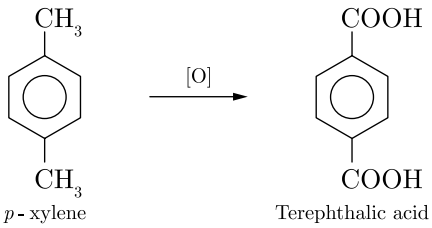
(vii) **From trihaloalkanes :**

$$CHCl_3 + 3KOH \xrightarrow{-3KCl} CH(OH)_3 \longrightarrow HCOOH + H_2O$$

(viii) **From alkyl benzenes :**

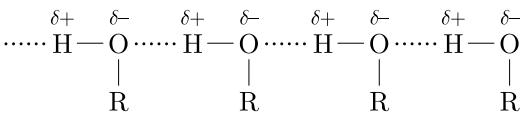


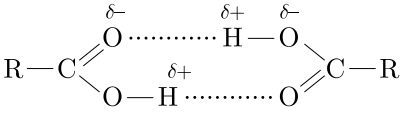




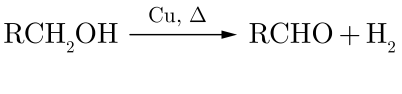
Physical properties of carboxylic acids :

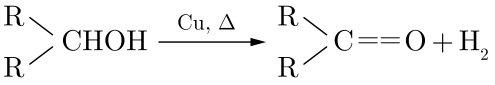
1. They are polar in nature from H-bonds and exist as dimers.
2. Lower members are soluble in water because they from H-bonds with water whereas the higher members are insoluble in water.
3. Monocarboxylic acids have higher boiling points than alcohols although both involve H-bonds. This is because in monocarboxylic acids :
   1. There are more number of H-bonds
   2. The hydrogen bonds are stronger than in alcohols due to greater polarity of -O-H bonds



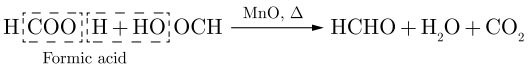


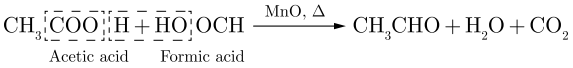
(b) **By dehydrogenation :**

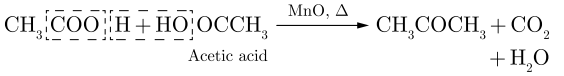




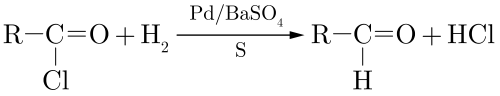
(ii) **From carboxylic acids :**



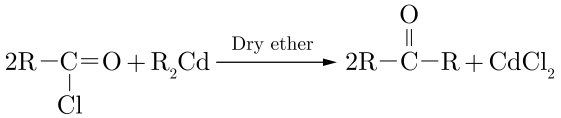




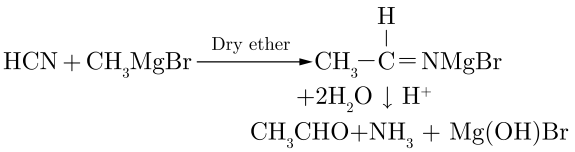
(iii) **From acid chloride (Rosenmund's reduction) (Name Reaction) :**



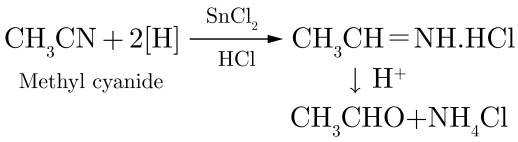
For ketones :



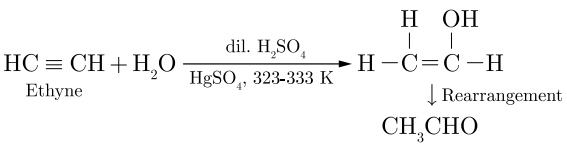
(iv) **From Grignard's reagent :**

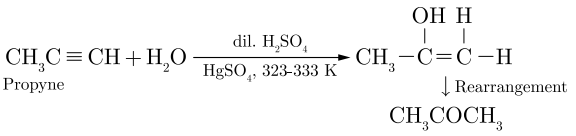


(v) **From alkyl cyanide (Stephen's reaction) (Name Reaction) :**

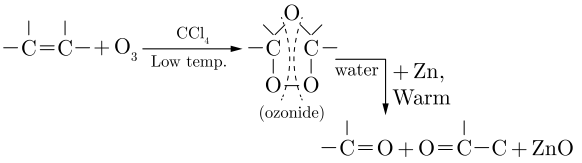


(vi) **From alkynes :**

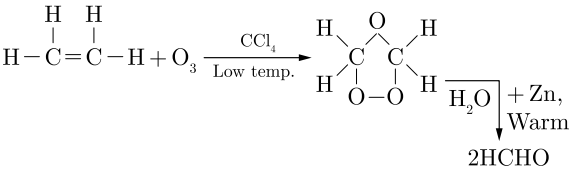




(vii) **From alkenes :**

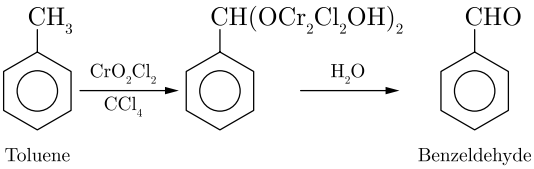


For example :

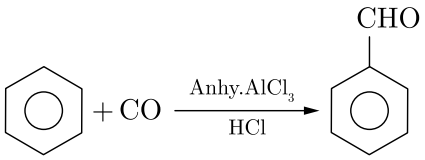


4. SPECIAL METHODS TO PREPARE AROMATIC ALDEHYDES AND KETONES

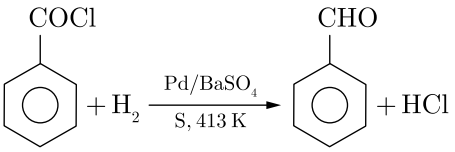
1. **Etard's reaction (Name reaction) :**



2. **Gattermann Koch reaction (Name Reaction):**



3. **Rosenmund's reaction (Name Reaction) :**



5. PHYSICAL PROPERTIES OF ALDEHYDES AND KETONES

Physical properties of aldehydes and ketones are as follows :

5.1 Solubility :

Lower aldehydes and ketones are soluble in water due to hydrogen bonding with water molecules. Solubility decreases as the size of the carbon chain increases.

5.2 Boiling Point

The boiling point of aldehydes and ketones are higher than non-polar (hydrocarbons) and weakly polar (ethers) compounds but lower than alcohols and carboxylic acids due to dipole-dipole interaction which is weaker force than H-bonding in alcohols and carboxylic acids.

6. CHEMICAL PROPERTIES OF ALDEHYDES AND KETONES

Chemical properties of aldehydes and ketones are as follows :

6.1 Relative Reactivity of Aldehydes and Ketones

Aldehydes are generally more reactive than ketones due to the electron releasing effect (+1 effect) of the alkyl group and steric effect of alkyl group.

6.2 Aromatic vs. Aliphatic Reactivity

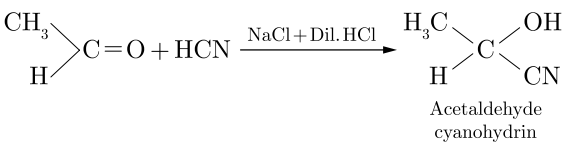
Aromatic aldehydes and ketones are less reactive than aliphatic aldehydes

and ketones due to resonance effect of benzene ring. The order of reactivity is :

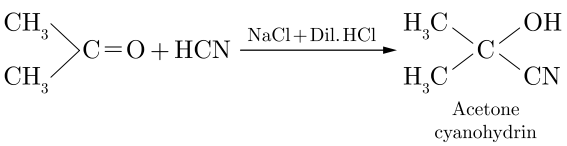
Aliphatic aldehydes > aromatic aldehydes > Aliphatic ketones > aromatic ketones.

1. Nucleophilic addition reaction :

(a) **With HCN :**

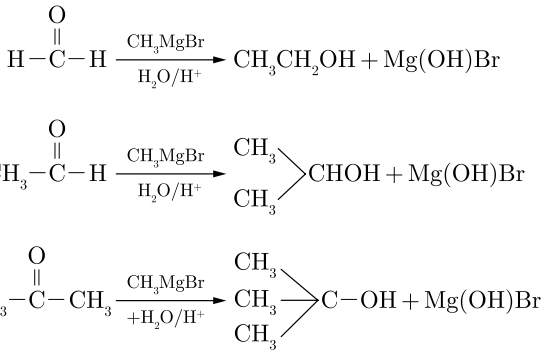


Acetaldehyde cyanohydrin

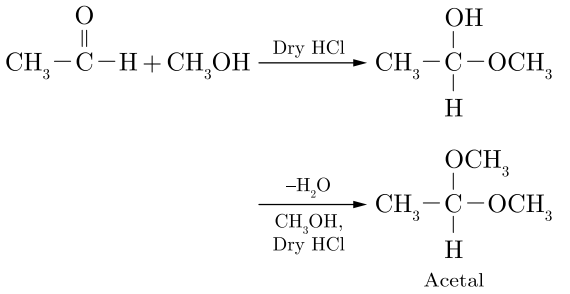


Acetone cyanohydrin

(b) **With Grignard reagent :**

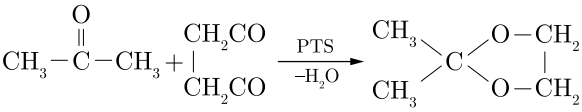


(c) **With alcohols :**



Acetal

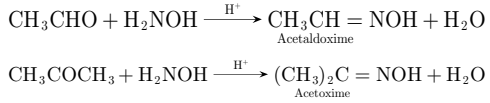
Ketones do not react with monohydric alcohols but they react with dihydric alcohols.



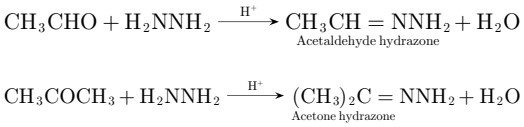
(Ketal)

(d) **With ammonia derivatives :**

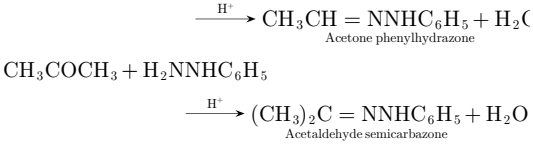
(i) **With hydroxylamine :**



(ii) **With hydrazine :**



(iii) **With phenylhydrazine :**



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(iv) **With semicarbazide :**

$$CH_3CHO + H_2NNHCONH_3 \xrightarrow{H^+} \underset{\text{Acetaldehyde semicarbazone}}{CH_3CHNNHCONH_2} + H_2O$$

$$CH_3COCH_3 + H_2NNHCONH_2 \xrightarrow{H^+} \underset{\text{Acetone semicarbazone}}{(CH_3)_2C=NNHCONH_2} + H_2O$$

(e) **With ammonia :**

$$6HCHO + 4NH_3 \longrightarrow (CH_2)_6N_4 + 6H_2O$$

$$CH_3CHO + NH_3 \longrightarrow CH_3CH(OH)NH_2 \xrightarrow[\Delta]{-H_2O} \underset{\text{Acetaldimine}}{CH_3CH=NH}$$

(f) **With primary amines :**

$$RCHO + RNH_2 \longrightarrow \underset{\text{Schiff's base}}{RCH=NR} + H_2O$$

2. Oxidation reaction :

$$RCHO \xrightarrow[KMnO_4/H_2SO_4]{[O]} RCOOH$$

$$RCOR \xrightarrow[KMnO_4/H_2SO_4]{[O]} RCOOH + CO_2 + H_2O$$

3. Reduction :

(i) Aldehydes and ketones are reduced by H_2 gas in the presence of Pt catalyst to give the corresponding alcohols. Aldehydes give primary alcohols and ketones give secondary alcohols.

$$RCHO + H_2 \xrightarrow{Pt.} RCH_2OH$$

$$\begin{matrix} R \\ R \end{matrix}\!\!>\!C=O + H_2 \xrightarrow{Pt.} \begin{matrix} R \\ R \end{matrix}\!\!>\!CHOH$$

(ii) **Clemmensen's reduction (Name Reaction) :** Aldehydes and ketones are reduced to the corresponding hydrocarbons by treatment with amalgamated zinc [Zn/Hg] and conc. HCl. The C=O group is completely reduced to $-CH_2-$.

$$CH_3CHO + 4[H] \xrightarrow[HCl]{Zn/Hg} CH_3 - CH_3 + H_2O$$

$$CH_3COCH_3 + 4[H] \xrightarrow[HCl]{Zn/Hg} CH_3CH_2CH_3 + H_2O$$

(iii) **Wolff-Kishner reduction (Name Reaction) :** Aldehydes and ketones are reduced to the corresponding hydrocarbons by treatment with hydrazine ($NH_2 \cdot NH_2$) followed by heating with KOH. The reaction proceeds through a hydrazone intermediate with evolution of N_2 gas.

$$CH_3CHO \xrightarrow[KOH]{NH_2NH_2} CH_3 - CH_3$$

$$CH_3COCH_3 \xrightarrow[KOH]{NH_2NH_2} CH_3CH_2CH_3$$

7. ALDOL CONDENSATION

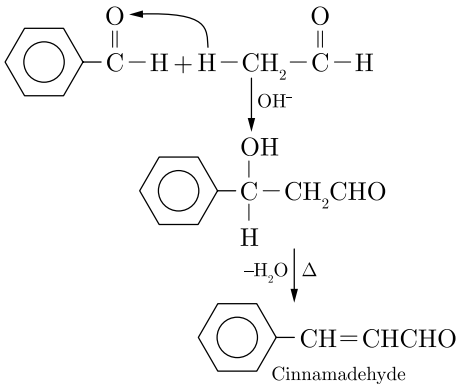
It takes place between two molecules of aldehydes or ketones having $\alpha - H$ atoms.

(i) $CH_3-\overset{\overset{O}{\uparrow}}{C}-H + HCH_2-\overset{O}{\overset{\|}{C}}-H \xrightarrow{NaOH} CH_3-\underset{H}{\overset{OH}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-H \xrightarrow[\Delta]{-H_2O} \underset{\text{Crotonaldehyde}}{CH_3-CH=CHCHO}$

(ii) $CH_3-\overset{\overset{O}{\uparrow}}{C}-CH_3 + HCH_2-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{NaOH} CH_3-\underset{CH_3}{\overset{OH}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[\Delta]{-H_2O} \underset{\text{Mesityl oxide}}{CH_3-\underset{CH_3}{C}=CHCOCH_3}$

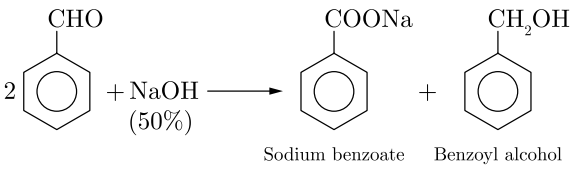
Cross aldol condensation or Claisen condensation (Name Reaction) :

This reaction is useful when one of the carbonyl compounds does not have an α-H atom.



Cannizzaro's reaction (Name Reaction) :

$$2HCHO + NaOH \longrightarrow HCOONa + CH_3OH$$



NODIA

13. A student observed that acetaldehyde undergoes self-condensation in presence of dilute alkali producing a beta-hydroxy aldehyde. Name the reaction involved.

ISC 2024

(a) Cannizzaro reaction

(b) Aldol condensation

(c) Perkin reaction

(d) Gattermann-Koch reaction

Ans : (b) Aldol condensation

Aldol condensation occurs in aldehydes and ketones possessing alpha hydrogen atoms. Acetaldehyde undergoes nucleophilic addition in presence of dilute alkali producing beta-hydroxy aldehyde called aldol. On heating, aldol further loses water forming crotonaldehyde. The reaction is important for carbon-carbon bond formation in organic synthesis.

14. A laboratory assistant reduced benzaldehyde using sodium borohydride. Which product was formed after completion of the reaction?

ISC 2009

(a) Benzoic acid

(b) Benzene

(c) Benzyl alcohol

(d) Benzophenone

Ans : (c) Benzyl alcohol

Sodium borohydride is a mild reducing agent that selectively reduces aldehydes into primary alcohols. During the reaction hydride ion attacks the electrophilic carbonyl carbon of benzaldehyde followed by protonation. As a result benzyl alcohol is produced without affecting the aromatic benzene ring.

15. A student heated toluene with chromyl chloride followed by hydrolysis and obtained an aromatic aldehyde. Identify the product formed.

ISC 2002

(a) Benzoic acid

(b) Benzaldehyde

(c) Benzyl alcohol

(d) Acetophenone

Ans : (b) Benzaldehyde

In Etard reaction, chromyl chloride selectively oxidises the methyl group of toluene into aldehyde group without further oxidation to carboxylic acid. Hydrolysis of the intermediate complex produces benzaldehyde. This reaction is especially important because direct oxidation of alkyl benzenes usually forms carboxylic acids instead of aldehydes.

16. During laboratory identification, a carbonyl compound reacted with semicarbazide forming crystalline derivative. Which functional group is confirmed by this test?

ISC 2021

(a) Carboxyl group

(b) Amino group

(c) Carbonyl group

(d) Hydroxyl group

Ans : (c) Carbonyl group

Aldehydes and ketones react with semicarbazide through nucleophilic addition followed by elimination of water forming semicarbazones. These derivatives are crystalline solids possessing characteristic melting points and are commonly used for identification of carbonyl compounds in qualitative organic analysis.

17. A chemist observed that benzaldehyde is less reactive than ethanal towards nucleophilic addition reactions. Which factor mainly decreases the reactivity of benzaldehyde?

ISC 2016

(a) Presence of hydrogen bonding

(b) Resonance with benzene ring

(c) Presence of ionic bond

(d) Absence of carbonyl group

Ans : (b) Resonance with benzene ring

In benzaldehyde, the carbonyl group is conjugated with the benzene ring. Resonance delocalises electron density reducing the partial positive charge on carbonyl carbon. Consequently nucleophilic attack becomes less favourable. Ethanal lacks such resonance stabilisation and therefore reacts more readily in nucleophilic addition reactions.

18. A student treated ethanal with hydrogen cyanide in presence of potassium cyanide. Which type of reaction occurred during the process?

ISC 2010

(a) Electrophilic substitution

(b) Nucleophilic addition

(c) Elimination reaction

(d) Free radical substitution

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4. Their acidic strength decreases with increases in molecular mass.

Chemical properties of carboxylic acids :

(i) With active metals :

$$2RCOOH + 2Na \longrightarrow 2RCOONa + H_2$$

(ii) **With carbonates :**

$$2RCOOH + Na_2CO_3 \longrightarrow 2RCOONa + CO_2 + H_2O$$

(iii) **With** PCl_3 **:**

$$3RCOOH + PCl_3 \longrightarrow RCOCl + H_3PO_3$$

(iv) With PCl_5

$$RCOOH + PCl_5 \longrightarrow RCOCl + POCl_3 + HCl$$

(v) **With alcohols :**

$$RCOOH + R'OH \xrightarrow{Conc.H_2SO_4} RCOOR' + H_2O$$

(vi) **With** NH_3 **:**

$$RCOOH + NH_3 \xrightarrow{\Delta} RCOONH_4 \longrightarrow RCONH_2 + H_2O$$

(vii) Decarboxylation :

$$RCOOH + NaOH \xrightarrow{CaO} RH + Na_2CO_3$$

(viii) **Reduction :**

$$RCOOH \xrightarrow{LiAlH_4} RCH_2OH + H_2O$$

$$RCOOH \xrightarrow{HI/P} R - R + 2H_2O + 3I_2$$

(ix) **Hell-Volhard Zelinsky reaction (Name Reaction):**

$$CH_3COOH \xrightarrow[-HCl]{Cl_2/P} \underset{\text{Monochloroacetic acid}}{ClCH_2COOH}$$

$$\xrightarrow[-HCl]{Cl_2/P} \underset{\text{Dichloroacetic acid}}{Cl_2CHCOOH}$$

$$- \xrightarrow[-HCl]{Cl_2/P} \underset{\text{Trichloriacetic acid}}{Cl_3CCOOH}$$

(x) **Kilbe's electrolysis (Name Reaction) :**

$$2CH_3COONa + 2H_2O \xrightarrow{Electrolysis} C_2H_2 + 2CO_2 + 2NaOH + H_2$$

Acidic Nature of Monocarboxylic acids

Presence of electron withdrawing substituents (e.g., $-Cl$, NH_2,$-NO_2$, $-C_6H_5$ etc.) increase their acidity.

Increase of number of electrons withdrawing substituents increases their acidity. Thus,

$$\underset{\text{Acetic acid}}{CH_3COOH} < \underset{\text{Monochloro acetic acid}}{ClCH_2COOH} < \underset{\text{Dichloro acetic acid}}{Cl_2COOH} < \underset{\text{Trichloro acetic acid}}{Cl_3CCOOH}$$

As the electron withdrawing substituent is move away from $-COOH$ group, the acidity rapidly diminishes.

$$\underset{\alpha\text{ - chlorobutyric acid}}{CH_3\overset{Cl}{\overset{|}{C}}H_2CHCOOH} > \underset{\beta\text{ - chlorobutyric acid}}{CH_3\overset{Cl}{\overset{|}{C}}HCH_2COOH} > \underset{\gamma\text{ - chlorobutyric acid}}{\overset{Cl}{\overset{|}{C}}HCH_2COOH}$$

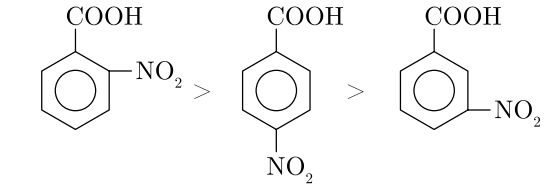
Acid strength of the halogen substituted carboxylic acid decreases as follows:

$$\underset{\text{Fluoroacetic acid}}{FCH_2COOH} > \underset{\text{Chloroacetic acid}}{ClCH_2COOH} > \underset{\text{Bromoacetic acid}}{BrCH_2COOH} > \underset{\text{Iodoacetic acid}}{ICH_3COOH}$$

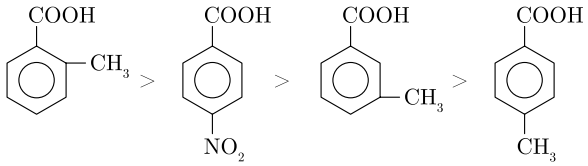
$$\underset{\text{Formic acid}}{HCOOH} > \underset{\text{Acetic acid}}{CH_3COOH} > \underset{\text{Propionic acid}}{C_2H_5COOH} > \underset{\substack{\text{2-methyl}\\\text{propionic acid}}}{(CH_3)_2CHCOOH}$$

$$> \underset{\substack{\text{2,2-dimethyl}\\\text{propionic acid}}}{(CH_3)_3CCOOH}$$

Ortho substituted aromatic carboxylic acids are stronger than para and meta substituted acids. Thus,



o - Nitrobenzoic acid | *p* - Nitrobenzoic acid | *m* - Nitrobenzoic acid



o - Toluic acid | Benzoic acid | *m* - Toluic acid | *p* - Toluic acid

OBJECTIVE QUESTIONS

1. Benzaldehyde undergoes ....'*A*'... reaction due to .... '*B*'.... of α-hydrogen atom.

In the above sentence, '*A*' and '*B*' respectively are

(a) Cannizzaro, absence

(b) Rosenmund, presence

(c) Cannizzaro, presence

(d) Rosenmund, absence

ISC 2016

Ans : (a) Cannizzaro, absence

Benzaldehyde undergoes Cannizzaro reaction on treatment with concentrated sodium hydroxide because it has no α-hydrogen (or absence of α -hydrogen) atom.

NODIA

2. When acetone is treated with Grignard reagent, followed by hydrolysis, the product formed is

ISC 2020

(a) secondary alcohol

(b) tertiary alcohol

(c) primary alcohol

(d) aldehyde

Ans : (b) tertiary alcohol

Acetone is a ketone. Grignard reagents (RMgX) add an alkyl group to the carbonyl carbon of ketones. After hydrolysis, the product formed is a tertiary alcohol because the carbon atom carrying the –OH group becomes attached to three carbon groups.

3. Iodoform test is given by

(a) formaldehyde (b) benzaldehyde

(c) methyl ketones (d) All of these

ISC 2012

Ans : (c) methyl ketones

Iodoform test is given by compounds that contain the methyl ketone group, written as $CH_3CO–$. These compounds react with iodine and alkali to form a yellow precipitate of iodoform (CHI_3), which has a characteristic smell. Since formaldehyde and benzaldehyde do not contain the $CH_3CO–$ group, they do not give the iodoform test.

4. Effervescence takes place when sodium carbonate solution is added to

ISC 2003

(a) formaldehye (b) acetaldehyde

(c) acetic acid (d) phenol

Ans : (c) acetic acid

Effervescence is observed when sodium carbonate reacts with an acid and releases carbon dioxide gas. Acetic acid reacts with sodium carbonate to produce sodium acetate, water, and carbon dioxide gas, which causes bubbling or effervescence. Formaldehyde, acetaldehyde and phenol do not react with sodium carbonate in this manner.

$$2CH_3COOH + Na_2CO_3 \rightarrow 2CH_3COONa + H_2O + CO_2$$

5. During decarboxylation reaction, sodium acetate was heated with soda lime. Which hydrocarbon was obtained?

ISC 2011

(a) Ethane

(b) Methane

(c) Propane

(d) Ethene

Ans : (b) Methane

Decarboxylation removes carbon dioxide from sodium salts of carboxylic acids when heated with soda lime. Sodium acetate loses one carbon atom forming methane.

$$CH_3COONa + NaOH \xrightarrow{CaO,\ \Delta} CH_4 + Na_2CO_3$$

The reaction is important for preparation of alkanes having one carbon atom less than the parent acid.

6. Benzaldehyde when heated with alcoholic solution of potassium cyanide gives

ISC 2021-22 (Sem-II)

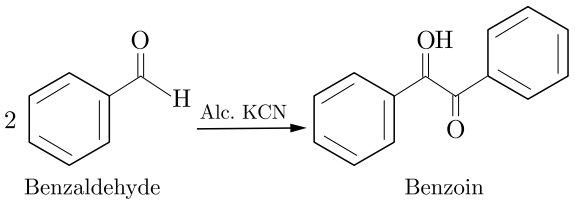
(a) $C_6H_5CH(OH)CN$

(b) $C_6H_5CH(OH)COC_6H_5$

(c) $C_6H_5CH(OH)COOH$

(d) $C_6H_5CH(OH)C_6H_5$

Ans : (b) $C_6H_5CH(OH)COC_6H_5$



7. A student added sodium bicarbonate solution to acetic acid and observed brisk effervescence. Which gas was evolved during the reaction?

ISC 2024

(a) Hydrogen

(b) Oxygen

(c) Carbon dioxide

(d) Sulphur dioxide

Ans : (c) Carbon dioxide

Carboxylic acids react with sodium bicarbonate producing sodium carboxylate, water and carbon dioxide gas.

$$CH_3COOH + NaHCO_3 \rightarrow CH_3COONa + CO_2 + H_2O$$

The brisk effervescence due to carbon dioxide evolution is an important distinguishing test for carboxylic acids because alcohols and phenols generally do not show this reaction.

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8. During qualitative analysis, a student added Tollens' reagent separately to ethanal and propanone. One compound produced a bright silver mirror while the other showed no visible change. Identify the compound that gives positive Tollens' test.

ISC 2009

(a) Propanone

(b) Ethanal

(c) Both ethanal and propanone

(d) Neither ethanal nor propanone

Ans : (b) Ethanal

Tollens' reagent is a mild oxidising agent that oxidises aldehydes into carboxylic acids. Ethanal contains hydrogen directly attached to the carbonyl carbon and therefore reduces silver ions to metallic silver producing a silver mirror. Ketones such as propanone generally resist oxidation under mild conditions and hence do not respond.

9. A chemist converted an acid chloride into the corresponding aldehyde using hydrogen gas in the presence of poisoned palladium catalyst. Which named reaction is involved in this transformation?

ISC 2017

(a) Stephen reaction

(b) Cannizzaro reaction

(c) Rosenmund reaction

(d) Etard reaction

Ans : (c) Rosenmund reaction

Rosenmund reduction converts acid chlorides into aldehydes using hydrogen gas in the presence of palladium catalyst poisoned with sulphur or barium sulphate. The poisoned catalyst prevents further reduction of aldehydes into alcohols. This method is particularly useful for selective preparation of aromatic and aliphatic aldehydes.

10. A carbonyl compound lacking alpha hydrogen atoms was treated with concentrated sodium hydroxide solution. The reaction produced alcohol and sodium salt of acid simultaneously. Which reaction explains this behaviour?

ISC 2018

(a) Aldol condensation

(b) Perkin reaction

(c) Cannizzaro reaction

(d) Friedel-Crafts reaction

Ans : (c) Cannizzaro reaction

Cannizzaro reaction occurs in aldehydes that do not possess alpha hydrogen atoms. Under strongly alkaline conditions, one molecule of aldehyde undergoes oxidation while another undergoes reduction. Consequently alcohol and carboxylate salt are formed together. Benzaldehyde and formaldehyde are common examples showing this reaction.

11. While comparing reactivity towards nucleophilic addition reactions, formaldehyde was found to react faster than acetone. Which factor mainly accounts for this observation?

ISC 2025

(a) Acetone possesses stronger sigma bond

(b) Formaldehyde contains no alkyl groups

(c) Acetone is an aromatic compound

(d) Formaldehyde is non-polar

Ans : (b) Formaldehyde contains no alkyl groups

Formaldehyde contains only hydrogen atoms attached to the carbonyl carbon and therefore experiences minimum steric hindrance and no electron donating inductive effect. Acetone contains two alkyl groups which decrease electrophilic character of carbonyl carbon and hinder nucleophilic attack. Hence formaldehyde reacts much faster than acetone.

12. During reduction of acetone using amalgamated zinc and concentrated hydrochloric acid, the carbonyl group was completely converted into methylene group. Which reaction is represented here?

ISC 2008

(a) Wolff-Kishner reduction

(b) Clemmensen reduction

(c) Rosenmund reduction

(d) Stephen reaction

Ans : (b) Clemmensen reduction

Clemmensen reduction converts aldehydes and ketones into hydrocarbons using zinc amalgam and concentrated hydrochloric acid. The carbonyl group is completely reduced into methylene group. This reaction is useful for compounds stable under acidic conditions and is widely employed in synthetic organic chemistry for deoxygenation of carbonyl compounds.

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CHAPTER 8

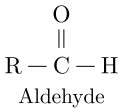
Aldehydes, Ketones and Carboxylic Acid

SUMMARY

1. CARBONYL GROUP

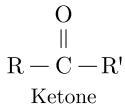
The functional group C=O (a carbon atom doubly bonded to an oxygen atom) is called the carbonyl group. It is one of the most important and widely occurring functional groups in organic chemistry.

Organic compounds containing the carbonyl group are aldehydes, ketones, carboxylic acids and their derivatives (acid chlorides, acid anhydrides, esters, amides, etc.). The general formulae of these compounds are :



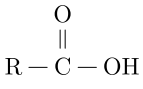
Aldehyde

(Where R may be H or any alkyl, aryl or aralkyl group)



Ketone

(Where R and R' may be same or different alkyl, aryl or aralkyl group)



Carboxylic acid

(Where R may be H or any alkyl, aryl or aralkyl group)

2. STRUCTURE OF ALDEHYDES AND KETONES

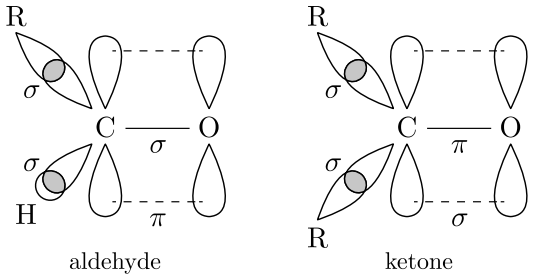
Aldehydes and ketones are the two most important classes of carbonyl compounds. In aldehydes, the carbonyl group is attached to at least one hydrogen atom (R–CHO), while in ketones, it is flanked by two carbon groups (R–CO–R'). Despite this structural difference, both classes share similar bonding characteristics at the carbonyl group due to sp^2 hybridisation of the carbonyl carbon. The structure and nature of the carbonyl group are described below.

2.1 Nature of the Carbonyl Group

Aldehydes and ketones are carbonyl compounds and contain the C=O (carbonyl) functional group. The carbonyl group consists of a carbon atom doubly bonded to an oxygen atom. The double bond is made up of one σ-bond and one π-bond.

2.2 Hybridisation of the Carbonyl Carbon

The carbon atom of the carbonyl group is sp^2 hybridised. The three sp^2 hybrid orbitals of the carbonyl carbon form three σ-bonds, while the remaining un-hybridised p-orbital forms the ϖ-bond with the oxygen atom.

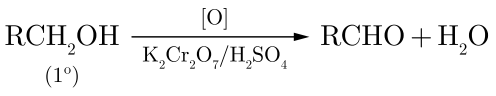


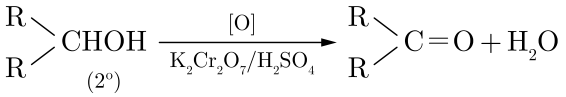
There is double bond between C and O made-up of a strong σ and weak π bond.

3. GENERAL METHODS OF PREPARATION OF ALDEHYDES AND KETONES

(i) **From alcohol :**

(a) **By oxidation :**





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Ans : (b) Nucleophilic addition

The carbonyl carbon in aldehydes possesses partial positive charge due to the electronegativity difference between carbon and oxygen. Cyanide ion attacks this electrophilic carbon forming cyanohydrin through nucleophilic addition mechanism. Such reactions are characteristic of aldehydes and ketones because the carbonyl group is highly polar in nature.

19. A chemist compared the boiling points of propanal and propanol having similar molecular masses. Propanol showed significantly higher boiling point. Which factor mainly explains this observation?

ISC 2025

(a) Propanal is non-polar

(b) Propanol forms intermolecular hydrogen bonding

(c) Propanol contains ionic bonds

(d) Propanal possesses stronger sigma bonds

Ans : (b) Propanol forms intermolecular hydrogen bonding

Alcohol molecules contain hydroxyl groups capable of forming strong intermolecular hydrogen bonds. Considerable energy is required to break these interactions during boiling. Aldehydes possess only dipole-dipole interactions due to polar carbonyl group. Since hydrogen bonding is much stronger than dipole interactions, propanol exhibits higher boiling point than propanal.

20. During reduction of acetone using hydrazine and potassium hydroxide, propane was obtained as the final product. Which named reaction is represented here?

ISC 2020

(a) Clemmensen reduction

(b) Rosenmund reduction

(c) Wolff-Kishner reduction

(d) Stephen reaction

Ans : (c) Wolff-Kishner reduction

Wolff-Kishner reduction converts aldehydes and ketones into hydrocarbons using hydrazine followed by heating with potassium hydroxide. The reaction proceeds through hydrazone intermediate with elimination of nitrogen gas. Since the reaction occurs in strongly basic medium, it is suitable for compounds unstable under acidic conditions.

21. A carbonyl compound reacted with hydroxylamine producing an oxime derivative. Which functional group is responsible for this reaction?

ISC 2007

(a) Hydroxyl group

(b) Carboxyl group

(c) Carbonyl group

(d) Ether linkage

Ans : (c) Carbonyl group

Aldehydes and ketones react with hydroxylamine through nucleophilic addition followed by elimination of water forming oximes. The reaction specifically involves the carbonyl functional group and is widely used in qualitative analysis for identification and characterisation of carbonyl compounds due to formation of stable crystalline derivatives.

22. During preparation of aromatic aldehydes, benzene was treated with carbon monoxide and hydrogen chloride in presence of anhydrous $AlCl_3$ and CuCl. Which reaction is involved?

ISC 2015

(a) Gattermann-Koch reaction

(b) Etard reaction

(c) Perkin reaction

(d) Cannizzaro reaction

Ans : (a) Gattermann-Koch reaction

Gattermann-Koch reaction introduces formyl group into benzene ring using carbon monoxide and hydrogen chloride in presence of anhydrous aluminium chloride and cuprous chloride catalysts. The reaction produces benzaldehyde through electrophilic substitution mechanism and is an important industrial method for synthesis of aromatic aldehydes.

23. A chemist observed that trichloroacetic acid is much stronger acid than acetic acid. Which factor mainly accounts for the increased acidity?

ISC 2006

(a) Presence of hydrogen bonding

(b) Positive inductive effect of chlorine

(c) Negative inductive effect of chlorine

(d) Increased molecular mass

Ans : (c) Negative inductive effect of chlorine

Chlorine atoms strongly withdraw electron density through negative inductive effect stabilising the

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of an alkali while benzaldehyde does not give this test.

66. How can acetaldehyde be converted into acetamide?

ISC 2009

Ans :

Acetaldehyde to acetamide

$$\underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow[K_2Cr_2O_7+H_2SO_4]{[O]} \underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{+NH_3}$$

$$\underset{\text{Ammonium acetate}}{CH_3COONH_4} \xrightarrow[-H_2O]{\Delta} \underset{\text{Acetamide}}{CH_3CONH_2}$$

67. Name the following reaction :

$$CH_3CHO + CH_3COCH_3 \xrightarrow{OH^-} CH_3CH(OH)CH_2COCH_3$$

ISC 2009

Ans :

The given reaction is crossed aldol condensation as it occurs between one aldehyde and one ketone having α-H atom.

68. How can acetyl chloride be converted into acetaldehyde? Write the balanced chemical equations and name the reaction involved.

ISC 2001

Ans :

Acetyl chloride is converted to acetaldehyde by reduction with hydrogen in the presence of a palladium catalyst support over barium sulphate.

$$CH_3COCl + H_2 \xrightarrow[BaSO_4]{Pd} CH_3CHO + HCl$$

69. Write the balanced chemical equation for the reaction of benzaldehyde with hydrogen cyanide.

ISC 2010

Ans :

$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} + \underset{\text{Hydrogen cyanide}}{HCN} \longrightarrow \underset{\text{Benzaldehyde cyanohydrin}}{C_6H_5-\underset{\displaystyle CN}{\overset{\displaystyle OH}{\underset{|}{\overset{|}{CH}}}}}$$

70. Give one test to distinguish between acetaldehyde and formaldehyde.

ISC 2021-22 (Sem-11), 2016

Ans :

When both are treated with iodine in presence of alkali, acetaldehyde gives ppt. of iodoform but formaldehyde does not.

$$CH_3CHO + 4NaOH + 3I_2 \rightarrow CHI_3 + HCOONa + 3NaI + 3H_2O$$

$$HCHO + 4NaOH + 3I_2 \rightarrow \text{No iodoform}$$

71. Write the formula of the product formed when formaldehyde reacts with ammonia and name the product.

ISC 2012

Ans :

Formaldehyde reacts with ammonia to form hexamethylene tetraamine. Also, known as urotropine.

$$\underset{\text{Formaldehyde}}{6HCHO} + 4NH_3 \xrightarrow{\Delta} \underset{\substack{\text{(Urotropine)}\\ \text{Hexamethylenetetraamine}}}{(CH_2)_6N_4} + 6H_2O$$

72. Complete the following reaction and name the reaction.

$$.... + 3I_2 + 4KOH \longrightarrow CHI_3 + CH_3\overset{-}{C}OO\overset{+}{K} + 3KI + 3H_2O$$

ISC 2012

Ans :

$$CH_3COCH_3 + 3I_2 + 4KOH \longrightarrow CHI_3 + CH_3\overset{-}{C}OO\overset{+}{K} + 3KI + 3H_2O$$

This reaction is called iodoform reaction.

73. Write the balanced chemical equation for the reaction when sucrose is warmed with concentrated nitric acid.

ISC 2007, 2000

Ans :

The balanced chemical equation is

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} \xrightarrow[\text{Conc. } HNO_3, V_2O_5]{18[O]} 6\begin{pmatrix} COOH \\ | \\ COOH \end{pmatrix} + 5H_2O$$

74. Give one test to distinguish between acetone and acetic acid.

ISC 2006

Ans :

Acetic acid when heated with ethyl alcohol in the presence of conc. H_2SO_4, it gives a fruity smell of an ester, ethyl ethanoate.

$$\underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Ethyl alcohol}}{C_2H_5OH} \xrightarrow[\text{Conc. } H_2SO_4]{\Delta \text{ with}} \underset{\text{Ethyl ethanoate}}{CH_3COOC_2H_5} + H_2O$$

While acetone does not give this test.

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29. Formaldehyde when reacts with CH_3MgI forms an additional product, which on hydrolysis gives

ISC 2022 (Sem-11)

(a) ethyl iodide (b) methyl alcohol

(c) methyl iodide (d) ethyl alcohol

Ans : (d) ethyl alcohol

Formaldehyde (HCHO) reacts with methyl magnesium iodide (CH_3MgI), a Grignard reagent, to form an addition compound. During hydrolysis, the addition product converts into ethyl alcohol (C_2H_5OH).

$$\underset{\text{Formaldehyde}}{HCHO} + CH_3MgI \xrightarrow{\text{Hydrolysis}} \underset{\text{Ethyl alcohol}}{CH_3CH_2OH}$$

$$CH_3CH_2OMgI + H_2O \rightarrow CH_3CH_2OH$$

Thus, the final product formed is ethyl alcohol.

30. A chemist reduced propanone using catalytic hydrogenation in presence of platinum catalyst. Which product was formed after the reaction?

ISC 2023

(a) Propanal

(b) Propane

(c) Propan-2-ol

(d) Propanoic acid

Ans : (c) Propan-2-ol

Ketones undergo catalytic hydrogenation in presence of metal catalysts such as platinum, palladium or nickel. Hydrogen adds across the carbonyl bond converting ketones into secondary alcohols. Thus propanone gets reduced to propan-2-ol. Aldehydes under similar conditions form primary alcohols instead of secondary alcohols.

31. A student attempted self aldol condensation using formaldehyde but no aldol product was obtained. What is the main reason behind this observation?

ISC 2002

(a) Formaldehyde is aromatic

(b) Formaldehyde lacks carbonyl group

(c) Formaldehyde does not contain alpha hydrogen atom

(d) Formaldehyde is non-polar

Ans : (c) Formaldehyde does not contain alpha hydrogen atom

Aldol condensation requires at least one alpha hydrogen atom adjacent to the carbonyl group for formation of enolate ion. Formaldehyde does not possess any alpha carbon and therefore lacks alpha hydrogen atoms. Consequently it cannot undergo aldol condensation and instead generally participates in Cannizzaro reaction under alkaline conditions.

32. When acetic acid reacts with calcium hydroxide and the product is distilled dry, the compound formed is

ISC 2012

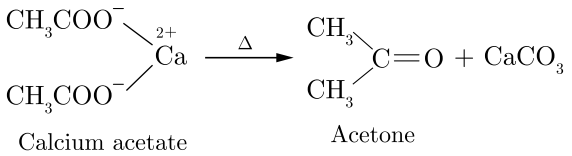
(a) calcium acetate (b) acetone

(c) acetaldehyde (d) acetic anhydride

Ans : (b) acetone

When (CH_3COOH) is treated with calcium hydroxide $[Ca(OH)_2]$ and product is distilled dry, the compound formed is acetone.

$$2CH_3COOH + Ca(OH)_2 \longrightarrow \underset{\text{Calcium acetate}}{(CH_3COO)_2Ca} + 2H_2O$$



Calcium acetate Acetone

33. During qualitative analysis, a student treated a carbonyl compound with phenylhydrazine and obtained yellow crystalline precipitate. Which derivative was formed?

ISC 2025

(a) Oxime

(b) Hydrazone

(c) Semicarbazone

(d) Cyanohydrin

Ans : (b) Hydrazone

Aldehydes and ketones react with phenylhydrazine through nucleophilic addition followed by elimination of water forming phenylhydrazones. These derivatives are generally yellow crystalline solids with sharp melting points. Such reactions are widely used for identification and characterisation of carbonyl compounds in practical organic chemistry.

34. While comparing acidic strengths, a student observed that formic acid is stronger than acetic acid. Which factor mainly explains this observation?

ISC 2020

(a) Acetic acid contains hydrogen bonding

(b) Methyl group exerts positive inductive effect

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carboxylate ion formed after proton removal. Greater the stabilisation of conjugate base, stronger becomes the acid. Trichloroacetic acid contains three chlorine atoms and therefore exhibits much greater acidic strength than acetic acid.

24. During laboratory preparation, acetylene was hydrated in presence of dilute sulphuric acid and mercuric sulphate catalyst. Which product was formed?

ISC 2022

(a) Ethanol

(b) Ethanal

(c) Ethanoic acid

(d) Acetone

Ans : (b) Ethanal

Hydration of acetylene initially forms unstable vinyl alcohol which rapidly undergoes tautomerism producing ethanal. The reaction occurs in presence of mercuric sulphate and dilute sulphuric acid catalyst. This method is important for industrial preparation of aldehydes from alkynes through electrophilic addition followed by rearrangement.

25. A student treated acetic acid with ethanol in presence of concentrated sulphuric acid. Which type of reaction occurred?

ISC 2017

(a) Reduction reaction

(b) Decarboxylation reaction

(c) Esterification reaction

(d) Polymerisation reaction

Ans : (c) Esterification reaction

Carboxylic acids react with alcohols in presence of concentrated sulphuric acid producing esters and water. Acetic acid and ethanol form ethyl ethanoate having pleasant fruity smell.

$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$

The reaction is reversible and commonly called esterification.

26. While studying acidity of substituted benzoic acids, a student found that ortho substituted benzoic acids are stronger than corresponding meta and para substituted acids. Which effect mainly explains this observation?

ISC 2005

(a) Hyperconjugation effect

(b) Ortho effect

(c) Steric inhibition effect

(d) Positive inductive effect

Ans : (b) Ortho effect

Ortho substituted benzoic acids generally exhibit greater acidity irrespective of the nature of substituent due to ortho effect. Steric crowding near the carboxyl group destabilises the undissociated acid more than the carboxylate ion. Consequently proton release becomes easier and acidity increases compared to corresponding meta and para substituted acids.

27. A laboratory assistant oxidised ethanol using acidified potassium dichromate solution. Initially an aldehyde was formed which on further oxidation produced a carboxylic acid. Identify the final product obtained.

ISC 2017

(a) Ethanal

(b) Ethene

(c) Ethanoic acid

(d) Acetone

Ans : (c) Ethanoic acid

Primary alcohols undergo oxidation first to aldehydes and then further to carboxylic acids in presence of strong oxidising agents such as acidified potassium dichromate. Ethanol initially forms ethanal which is further oxidised to ethanoic acid. The reaction demonstrates the characteristic oxidation behaviour of primary alcohols.

28. During an organic conversion experiment, a student treated benzaldehyde with concentrated sodium hydroxide solution. Which pair of products was formed?

ISC 2013

(a) Benzene and sodium benzoate

(b) Benzyl alcohol and sodium benzoate

(c) Benzoic acid and ethanol

(d) Benzophenone and methanol

Ans : (b) Benzyl alcohol and sodium benzoate

Benzaldehyde does not possess alpha hydrogen atoms and therefore undergoes Cannizzaro reaction in concentrated alkali. One molecule gets oxidised to sodium benzoate while another molecule gets reduced to benzyl alcohol. This disproportionation reaction is characteristic of aldehydes lacking alpha hydrogen atoms.

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Ans : (d) basic, anionic hydrolysis

An aqueous solution of sodium acetate (CH_3COONa) is basic in nature because it is a salt of a weak acid (CH_3COOH) and a strong base (NaOH). In water, the acetate ion (CH_3COO^-) undergoes anionic hydrolysis to produce hydroxide ions (OH^-), making the solution basic.

Therefore:

A = basic

B = anionic hydrolysis

40. When oxalic acid is heated with glycerol, we get

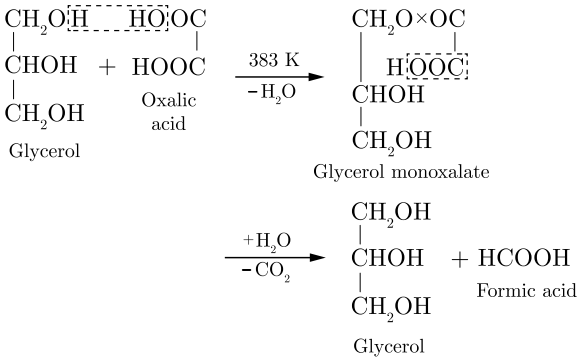
ISC 2009

(a) formic acid (b) acetic acid

(c) lactic acid (d) tartaric acid

Ans : (a) formic acid

When oxalic acid is heated with glycerol then we get formic acid.



41. When acetaldehyde is treated with Grignard reagent, followed by hydrolysis the product formed is

(a) primary alcohol

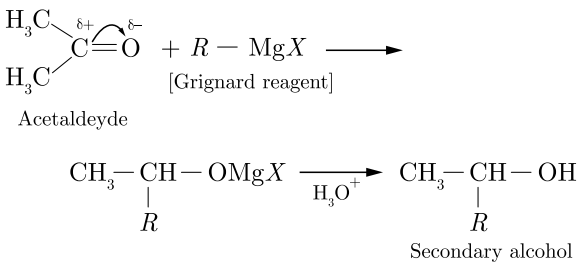
(b) secondary alcohol

(c) carboxylic acid

(d) tertiary alcohol

ISC 2015

Ans : (b) secondary alcohol



42. The compound which gives a positive haloform test and a positive Fehling solution test is

(a) acetone (b) acetaldehyde

(c) formaldehyde (d) diethyl ether

ISC 2007

Ans : (b) acetaldehyde

The compounds which have $CH_3-\overset{\overset{O}{\|}}{C}-$ group, give iodoform (haloform test). The compounds which have – CHO group (aldehyde) give Fehling solution test.

Among the given options, the compound which gives a positive haloform test and a positive Fehling solution test is acetaldehyde, because it has both $CH_3-\overset{\overset{O}{\|}}{C}-$ group and – CHO group.

43. Calcium acetate on heating gives ....'*A*'.... which gives ... '*B*' .... on heating with iodine and sodium hydroxide solution. In the above sentence, '*A*' and '*B*' are

(a) aldehyde, chloroform

(b) acetone, iodoform

(c) aldehyde, iodoform

(d) acetone, iodine tincture

ISC 2017

Ans : (b) acetone, iodoform

When calcium acetate is heated, it undergoes dry distillation to form acetone.

Reaction:

$$(CH_3COO)_2Ca \xrightarrow{\Delta} CH_3COCH_3 + CaCO_3$$

Acetone is a methyl ketone and gives the iodoform test with iodine and sodium hydroxide solution, producing yellow crystals of iodoform

Therefore:

A = acetone

B = iodoform

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83. How will you distinguish between acetone and phenol by a chemical test?

ISC 2013

Ans :

Acetone gives iodoform test while phenol does not. Acetone gives a yellow ppt. of iodoform when heated with I_2 in the presence of an alkali, while phenol does not contain $CH_3-\underset{\underset{O}{\|}}{C}-$ group, so do not give this test.

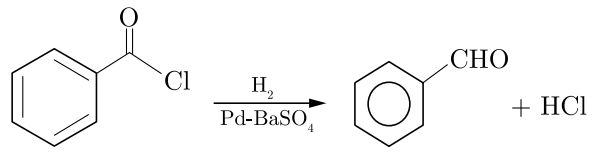
$$CH_3COCH_3 \xrightarrow{I_2/Na_2CO_3} \underset{\text{Triiodoacetonoe}}{I_3CCOCH_3} \xrightarrow{NaOH}$$

$$\underset{\text{Sodium acetate}}{CH_3COO^-Na^+} + \underset{\text{Iodoform}}{CHI_3}$$

84. How will you convert benzoyl chloride to benzaldehyde?

ISC 2020

Ans :



Benzoyl chloride Benzaldehyde

85. Give balanced equations for aldol condensation.

ISC 2019, 2017

Ans :

Aldehydes and ketones containing α-H-atoms undergo aldol condensation in presence of dilute alkali as catalyst.

$$\text{e.g. } \underset{\text{Ethanol}}{2CH_3-CHO} \xrightarrow{\text{Dil. NaOH}} \underset{\substack{\text{3-hydroxybutanal}\\\text{(Aldol)}\\\text{(Aldol condensation product)}}}{CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-CHO}$$

86. How will you distinguish between benzaldehyde and acetic acid by a chemical test?

ISC 2021-22 (Sem-II)

Ans :

Benzaldehyde reduces Tollen's reagent to give shining silver mirror but acetic acid does not.

$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} + 2\underset{\text{Tollen's reagent}}{[Ag(NH_3)_2]^+} + 3OH^- \longrightarrow$$

$$C_6H_5COO^- + \underset{\text{Silver mirror}}{2Ag\downarrow} + 2H_2O + 4NH_3$$

$$CH_3COOH \xrightarrow{\text{Tollen's reagent}} \text{No reaction}$$

87. Give chemical test to distinguish acetaldehyde and acetic acid.

ISC 2017

Ans :

Tollen's test Acetaldehyde reduces Tollen's reagent to give shining silver mirror but acetic acid does not.

$$\underset{\text{Acetaldehyde}}{CH_3CHO} + 2\underset{\text{Tollen's reagent}}{[Ag(NH_3)_2]^+} + 3OH^- \longrightarrow$$

$$\underset{\text{Acetate ion}}{CH_3COO^-} + \underset{\text{Silver mirror}}{2Ag\downarrow} + 2H_2O + 4NH_3$$

$$\underset{\text{Tollen's reagent}}{CH_3COOH} \longrightarrow \text{No reaction}$$

88. Write one example of the Benzoin condensation reaction.

ISC 2019, 2008

Ans :

When aromatic aldehydes react with ale. KCN, undergo self-condensation reaction it is called benzoin condensation. For example, benzaldehyde on heating with alc. KCN forms benzoin.

$$\underset{\text{Benzaldehyde}}{2C_6H_5CHO} \xrightarrow[\Delta]{\text{alc.KCN}} C_6H_5-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-\overset{\overset{O}{\|}}{C}-C_6H_5$$

(Benzoin)

89. Give one example for the following name reaction: Hell-Volhard-Zelinsky (HVZ) reaction.

ISC 2010

Ans :

$$\underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow[-HCl]{Cl_2,\text{Red P}} \underset{\text{Monochloro acetic acid}}{CH_2ClCOOH} \xrightarrow[(-HCl)]{Cl_2,\text{Red P}}$$

$$\underset{\substack{\text{Dichloro}\\\text{acetic acid}}}{CHCl_2COOH} \xrightarrow[-HCl]{Cl_2,\text{Red P}} \underset{\substack{\text{Trichloro}\\\text{acetic acid}}}{CCl_3COOH}$$

90. Give a chemical test to distinguish between acetaldehyde and acetone.

ISC 2007, 2000

Ans :

Acetaldehyde and acetone Acetaldehyde gives a silver mirror test when heated with Tollen's reagent.

$$\underset{\text{Acetaldehyde}}{CH_3CHO} + 2\underset{\substack{\text{Tollen's}\\\text{reagent}}}{[Ag(NH_3)_2]^+OH^-} \longrightarrow CH_3COONH_4$$

$$+ \underset{\text{Silver miror}}{2Ag} + 3NH_3 + H_2O$$

Acetone does not give this test as it is a ketone.

NODIA

55. How will acetone be converted into iodoform?

ISC 2021-22 (Sem-11)

Ans :

$$\underset{\text{Acetone}}{CH_3-COCH_3} \xrightarrow{I_2/Na_2CO_3} \underset{\text{Triodoacetone}}{I_3CCOCH_3} \xrightarrow{NaOH} \underset{\text{Iodoform}}{CHI_3} + \underset{\text{Sodium acetate}}{CH_3COO^-Na^+}$$

56. Write the balanced chemical equation for the reaction of acetic acid with phosphorus pentachloride.

ISC 2019

Ans :

Acetic acid reacts with phosphorus pentachloride

$$CH_3COOH + PCl_3 \rightarrow CH_3COCl + POCl_3 + HCl$$

57. How will you convert 2-propanol into acetoxime?

ISC 2010

Ans :

2-propanol to acetoxime

$$\underset{2-\text{Propanol}}{CH_3CHOHCH_3} \xrightarrow[O_2,\,573\,K]{Cu} \underset{\text{Acetone}}{CH_3COCH_3} \xrightarrow{+NH_2OH} \underset{\text{Acetoxime}}{(CH_3)_2C=NOH} + H_2O$$

58. Chloroacetic acid is more acidic than acetic acid because of the –I (electron withdrawing inductive) effect of chlorine.

ISC 2007

Ans :

The correct statement is Chloroacetic acid is more acidic than acetic acid due to the electron-withdrawing (-I) inductive effect of chlorine, which increases the release of H^+ ions.

59. Write the relevant chemical equations for the conversion of acetic acid into acetone.

ISC 2006

Ans :

The relevant chemical equations are

$$\underset{\text{Acetic acid}}{2CH_3COOH} + Ca(OH)_2 \longrightarrow \underset{\text{Calcium acetate}}{(CH_3COO)_2Ca} + 2H_2O$$

$$(CH_3COO)_2Ca \xrightarrow{\Delta} \underset{\text{Acetone}}{CH_3COCH_3} + CaCO_3\downarrow$$

60. Write the chemical equation for the reaction of formaldehyde with ammonia and name the main product formed.

ISC 2005

Ans :

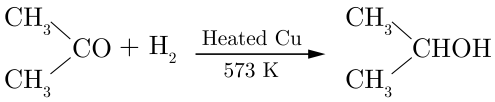
$$\underset{\text{Formaldehyde}}{6HCHO} + 4NH_3 \xrightarrow{\Delta} \underset{\text{Urotropine}}{(CH_2)_6N_4} + 6H_2O$$

Urotropine is formed.

61. Write the balanced chemical equation for the reaction of acetone with hydrogen in the presence of heated copper.

ISC 2011

Ans :

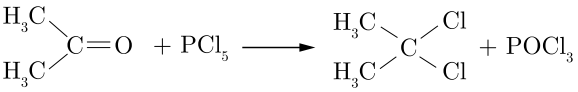


Acetone *Iso*-propyl alcohol

62. Write the balanced chemical equation for the reaction between acetone and phosphorus pentachloride.

ISC 2008

Ans :



2, 2-dichloropropane

63. Write the balanced chemical equation and identify the name reaction when benzaldehyde is treated with 50% sodium hydroxide solution.

ISC 2013, 2002

Ans :

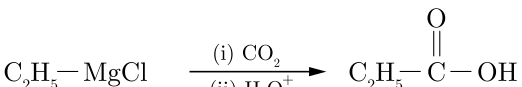
$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} + C_6H_5CHO \xrightarrow{50\%\ NaOH} \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} + \underset{\text{Sodium benzoate}}{C_6H_5COO^-Na^+}$$

This reaction is known as Cannizzaro reaction.

64. Starting with Grignard's reagent, how will you prepare propanoic acid?

ISC 2016

Ans :



Grignard's reagent Propanoic acid

65. Give one good chemical test to distinguish between the following pair of organic compounds :

Benzaldehyde and acetone

ISC 2011

Ans :

Due to the presence of CH_3CO- group acetone gives iodoform test, i.e. it gives a yellow ppt. of iodoform when heated with iodine in the presence

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FILL IN THE BLANK

44. Benzaldehyde undergoes _____ substitution at _____ position.

ISC 2021-22 (Sem-11)

Ans :

electrophilic, metal

45. Acetaldehyde in the presence of dilute alkali gives _____ and the reaction is called _____.

ISC 2005

Ans :

Acetaldehyde in the presence of dilute alkali gives aldol and the reaction is called aldol condensation.

46. _____ is more acidic than acetic acid because of _____ effect.

ISC 2003

Ans :

Benzoic acid is more acidic than acetic acid because of negative inductive effect ($-$I- effect is due to the presence of benzene ring.)

47. Benzaldehyde when treated with an alcoholic solution of _____ forms _____ .

ISC 2013

Ans :

Benzaldehyde when treated with an alcoholic solution of potassium cyanide forms benzoin.

48. Calcium acetate on dry distillation gives _____ which gives _____ on heating with iodine and alkali.

ISC Specimen 2023

Ans :

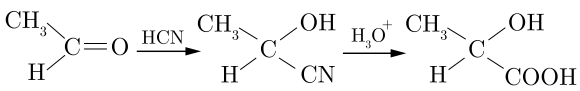
acetone, iodoform

49. Acetaldehyde reacts with HCN to give _____ which on hydrolysis gives _____.

ISC 2008

Ans :

Acetaldehyde reacts with HCN to give acetaldehyde cyanohydrin which on hydrolysis gives lactic acid.



Acetaldehyde Acetaldehyde cyanohydrin Lactic acid

50. Benzaldehyde undergoes _____ reaction on treatment with concentrated sodium hydroxide because it has _____.

ISC 2001

Ans :

Benzaldehyde undergoes Cannizzaro reaction on treatment with concentrated sodium hydroxide because it has no α-hydrogen atoms.

$$\underset{\text{Benzaldehyde}}{2C_6H_5CHO} + \underset{\text{Conc.}}{NaOH} \longrightarrow \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} + \underset{\text{Sodium benzoate}}{C_6H_5COONa}$$

ONE MARK QUESTIONS

51. The aqueous solution of sodium acetate is basic. Explain.

ISC 2015

Ans :

Because, when it reacts with water, it produces strong base, i.e. NaOH which makes the solution basic.

52. How will you distinguish between oxalic acid and benzoic acid by a chemical test?

ISC 2010

Ans :

Oxalic acid decolourised hot solution of acidified $KMnO_4$ whereas benzoic acid does not give this test.

53. Suggest one chemical test to distinguish between oxalic acid and acetic acid.

ISC 2009

Ans :

Oxalic acid decolourises acidified potassium permanganate solution while acetic acid does not.

$$2MnO_4 + 16H^+ + 5C_2O_4^{2-} \longrightarrow Mn^{2+} + 8H_2O + 10CO_2$$

54. Give balanced equation for the reaction of acetaldehyde with hydroxylamine.

ISC 2017

Ans :

$$\underset{\text{Acetaldehyde}}{CH_3CHO} + \underset{\text{Hydroxylamine}}{NH_2OH} \longrightarrow CH_3 - CH{=}NOH + H_2O$$

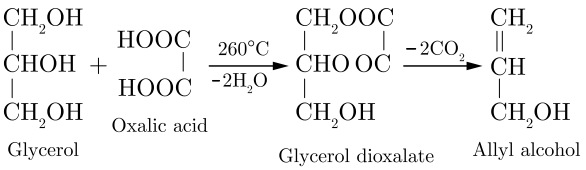
NODIA

75. Write the chemical equation for the reaction of oxalic acid with glycerol at 260C and name the main product formed.

ISC 2005

Ans :

Allyl alcohol is formed as :

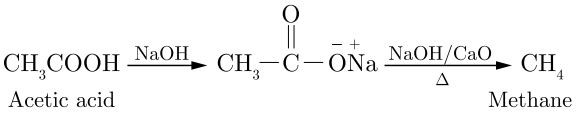


76. How can acetic acid be converted into methane?

ISC 2002

Ans :

When acetic acid is treated with caustic soda, it produces sodium salt of acetic acid. When it is refluxed in the presence of slaked lime, hydrocarbon is produced.

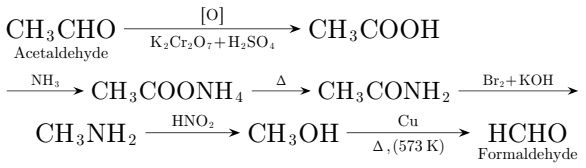


77. How can the following conversions be brought about?

Acetaldehyde to formaldehyde

ISC 2014

Ans :

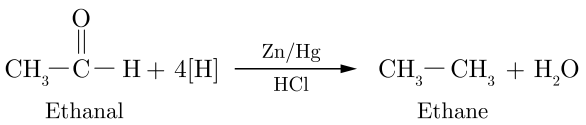


78. Write the balanced chemical equation for the Benzoin condensation reaction.

ISC 2014, 2010

Ans :

Reduction of acetaldehyde to ethane using Zn/Hg and HCl as reducing agent is an example of Clemmensen's reduction. The reaction involve is as follows.



79. Give the balanced equation for the following reaction: Formic acid is heated with Tollen's reagent.

ISC 2009

Ans :

$$\underset{\text{Formic acid}}{HCOOH} + 2[Ag(NH_3)_2]^+NO_3^- + H_2O \longrightarrow 2NH_4NO_3 + (NH_4)_2CO_3 + \underset{\text{Silver mirror}}{2Ag\downarrow}$$

Tollen's reagent $= [Ag(NH_3)_2]^+NO_3^-$

80. How will you convert ethanol into acetone?

ISC 2011

Ans :

Ethanol to acetone :

$$\underset{\text{Ethanol}}{2CH_3CH_2OH} \xrightarrow[K_2Cr_2O_7+H_2SO_4]{[O]} 2CH_3CHO \xrightarrow[K_2Cr_2O_7+H_2SO_4]{[O]}$$

$$\underset{\text{Acetic acid}}{2CH_3COOH} \xrightarrow{Ca(OH)_2} \underset{\text{Calcium acetate}}{(CH_3COO)_2Ca} \xrightarrow{\Delta}$$

$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + CaCO_3\downarrow$$

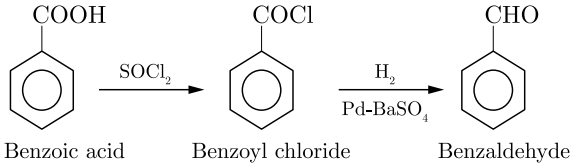
Acetone

81. How can the following conversion be brought about? Benzoic acid to benzaldehyde.

ISC 2013

Ans :

Benzoic acid is converted into benzaldehyde through the following steps.



82. How will you distinguish between formic acid and acetic acid by a chemical test?

ISC 2013

Ans :

Formic acid gives silver mirror test with Tollen's reagent while acetic acid does not give this test.

$$\underset{\text{Formic acid}}{HCOOH} + 2[Ag(NH_3)_2]^+NO_3^- + H_2O \longrightarrow 2NH_4NO_3 + (NH_4)_2CO_3 + \underset{\text{Silver mirror}}{2Ag\downarrow}$$

$$\underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Tollen's reagent}}{2[Ag(NH_3)_2]^+NO_3^-} + H_2O \longrightarrow \text{No reaction}$$

NODIA

(c) Formic acid is aromatic

(d) Acetic acid contains weaker carbonyl bond

Ans : (b) Methyl group exerts positive inductive effect

The methyl group in acetic acid donates electron density through positive inductive effect destabilising the acetate ion formed after proton loss. Consequently proton removal becomes comparatively difficult. Formic acid lacks electron donating alkyl groups and therefore its conjugate base remains relatively more stable, making formic acid stronger.

35. During preparation of aldehydes from nitriles, an alkyl cyanide was reduced using stannous chloride and hydrochloric acid followed by hydrolysis. Which named reaction is represented?

ISC 2019

(a) Rosenmund reaction

(b) Etard reaction

(c) Stephen reaction

(d) Gattermann-Koch reaction

Ans : (c) Stephen reaction

Stephen reaction converts nitriles into aldehydes using stannous chloride and hydrochloric acid. Initially iminium salt is formed which on hydrolysis produces aldehyde. This method is useful for preparation of aldehydes containing one additional carbon atom compared to the starting alkyl cyanide compound.

36. A student observed that benzoic acid exists as dimers in benzene solution. Which intermolecular force is mainly responsible for this behaviour?

ISC 2003

(a) Dipole-dipole interaction

(b) Ionic bonding

(c) Hydrogen bonding

(d) Covalent bonding

Ans : (c) Hydrogen bonding

Carboxylic acid molecules associate through strong intermolecular hydrogen bonding between hydroxyl hydrogen and carbonyl oxygen atoms. Two molecules combine forming cyclic dimers especially in non-polar solvents such as benzene. Presence of dimers increases boiling points and influences many physical properties of carboxylic acids.

General reaction :

CH_3COCH_3 + RMgX → tertiary alcohol after hydrolysis.

37. When acetaldehyde is treated with Grignard reagent followed by hydrolysis, the product formed is

ISC Specimen 2018

(a) primary alcohol

(b) secondary alcohol

(c) carboxylic acid

(d) tertiary alcohol

Ans : (b) secondary alcohol

$$\underset{\text{Acetaldehyde}}{CH_3-CHO} + RMgX \xrightarrow[(ii)\,H_2O/H^+]{(i)\text{ Dry ether}} \underset{\substack{\text{(Secondary alcohol)}\\(2^\circ)}}{H_3C-\overset{\overset{H}{|}}{\underset{\underset{R}{|}}{C}}-OH} + Mg(OH)X$$

38. A student treated acetic acid with phosphorus pentachloride during an organic conversion experiment. Which product was obtained?

ISC 2024

(a) Acetaldehyde

(b) Acetyl chloride

(c) Acetic anhydride

(d) Ethanol

Ans : (b) Acetyl chloride

Carboxylic acids react with phosphorus pentachloride replacing hydroxyl group by chlorine atom and forming acid chlorides.

$CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$

The reaction is commonly used for preparation of acid chlorides because these compounds are highly reactive intermediates in organic synthesis.

39. An aqueous solution of $CH_3COO\overset{-}{}\overset{+}{N}a$ is .....'*A*'.... due to .....'*B*'.....

In the above sentence, '*A*' and '*B*' are

ISC 2017

(a) acidic, anionic hydrolysis

(b) basic, cationic hydrolysis

(c) acidic, cationic hydrolysis

(d) basic, anionic hydrolysis

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91. How will you bring about the following conversion? Formic acid to oxalic acid.

ISC 2008, 2003

Ans :

$$\underset{\text{Formic acid}}{HCOOH} + NaOH \longrightarrow HCOO^{-}Na^{+} + H_2O$$

$$2HCOO^{-}Na^{+} \xrightarrow{390^\circ C} \underset{\text{Sodium formate}}{(COONa)_2} + H_2\uparrow$$

$$\underset{\text{Sodium oxalate}}{(COONa)_2} + CaCl_2 \longrightarrow \underset{\text{Calcium oxalate}}{(COO)_2Ca} + 2NaCl$$

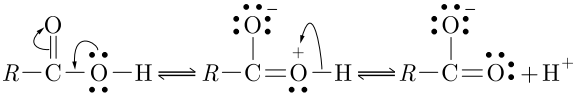
$$(COO)_2Ca + \underset{\text{(dil.)}}{H_2SO_4} \longrightarrow \underset{\text{Oxalic acid}}{(COOH)_2} + CaSO_4\downarrow$$

92. Explain, why acetic acid is a weaker acid as compared to formic acid ?

ISC 2018

Ans :

Acetic acid is a weaker acid as compared to formic acid because in acetic acid $-CH_3$ group acts as electron donating group. It decreases the stability of carboxylate ion by intensifying the negative charge and hence, decreases the acidity of carboxylic acid.



93. Write the chemical equations illustrating the HVZ reaction

ISC 2018

Ans :

Hell-Volhard-Zelinsky (HVZ) reaction :

$$\underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow[-HCl]{Cl_2,\text{Red P}} \underset{\substack{\text{Monochloro}\\\text{acetic acid}}}{CH_3ClCOOH} \xrightarrow[(-HCl)]{Cl_2,\text{Red P}}$$

$$\underset{\substack{\text{Dichloro}\\\text{acetic acid}}}{CHCl_2COOH} \xrightarrow[-HCl]{Cl_2,\text{Red P}} \underset{\substack{\text{Trichloro}\\\text{acetic acid}}}{CCl_3COOH}$$

94. Give one good chemical test to distinguish between the following pair of compounds.

Methanal and ethanal

ISC 2012

Ans :

Methanal and ethanal Ethanal when heated with I_2 and NaOH, it gives a yellow ppt. of iodoform.

$$\underset{\text{Ethanal}}{CH_3CHO} + 3I_2 + 4NaOH \longrightarrow \underset{\substack{\text{Iodoform}\\\text{(Yellow ppt.)}}}{CHI_3}\downarrow + HCOO^{-}Na^{+} + 3NaI + 3H_2O$$

$$\underset{\text{Methanal}}{HCHO} + 3I_2 + 4NaOH \longrightarrow \text{No reaction}$$

(Due to absence of CH_3CO- group)

95. Write the reaction to prepare acetaldehyde from hydrogen gas and an acid chloride.

ISC 2016

Ans :

Acid chloride (e.g. acetyl chloride) can be reduced to aldehyde (e.g. acetaldehyde) with hydrogen gas in boiling xylene using palladium as catalyst supported by $BaSO_4$ and partially poisoned by the addition of sulphur.

$$\underset{\text{Acetyl chloride}}{CH_3-\overset{\overset{O}{\|}}{C}-Cl} + H_2 \xrightarrow[\text{Boiling xylene}]{Pd/BaSO_4,\ S} \underset{\text{Acetaldehyde}}{CH_3-\overset{\overset{O}{\|}}{C}-H} + HCl$$

96. How will you carry out the following conversion?

Acetaldehyde to iso -propyl alcohol

ISC 2002, 2000

Ans :

$$\underset{\text{Acetaldehyde}}{CH_3-\overset{\overset{O}{\|}}{C}-H} \xrightarrow{CH_3MgI} CH_3-\overset{\overset{OMgI}{|}}{\underset{\underset{CH_3}{|}}{C}}-H \xrightarrow{H_2O}$$

$$CH_3-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-H + Mg\begin{matrix}OH\\I\end{matrix}$$

Iso-propyl alcohol

97. Give one chemical test to distinguish between the following pairs of compounds.

Acetaldehyde and benzaldehyde

ISC 2015

Ans :

Acetaldehyde and benzaldehyde Acetaldehyde reacts as reducing agent which reduces Fehling solution and itself gets oxidised to carboxylate ion and Cu^{2+} is reduced to cuprous oxide.

$$\underset{\text{Acetaldehyde}}{CH_3-\overset{\overset{O}{\|}}{C}-H} + 2Cu^{2+} + 5OH^{-} \longrightarrow \left[\underset{\text{Carboxylate ion}}{CH_3-\overset{\overset{O}{\|}}{C}-O}\right]^{-} + Cu_2O$$

Benzaldehyde is not oxidised by Fehling solution.

NODIA

135. Identify the compounds A, B and C.

(i) $C_2H_5OH \xrightarrow{PCl_5} [A] \xrightarrow{KCN} [B] \xrightarrow{H_3O^+} C_2H_5COOH \xrightarrow[\Delta]{NH_3} [C]$

(ii) $C_6H_5COOH \xrightarrow{SOCl_2} [A] \xrightarrow{NH_3} [B] \xrightarrow{Br_2/KOH} [C]$

ISC 2016

Ans :

(i) $C_2H_5OH \xrightarrow{PCl_5} \underset{(A)}{C_2H_5Cl} + POCl_3 + HCl$

$C_2H_5Cl \xrightarrow{KCN} \underset{(B)}{C_2H_5CN} \xrightarrow{H_3O^+} C_2H_5COOH$

$C_2H_5COOH \xrightarrow[\Delta]{NH_3} \underset{(C)}{C_2H_5COONH_4}$

(ii) $\underset{\text{Benzoic acid}}{C_6H_5COOH} \xrightarrow{SOCl_2} \underset{\substack{\text{Benzoyl chloride}\\(A)}}{C_6H_5COCl} + HCl + SO_2$

$\downarrow NH_3$

$\underset{\substack{\text{Benzamide}\\(B)}}{C_6H_5CONH_2} \xrightarrow{KOH/Br_2} \underset{\substack{\text{Aniline}\\(C)}}{C_6H_5NH_2}$

136. Give balanced chemical equations for the following reactions.

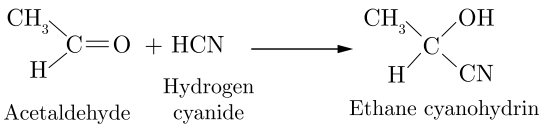
ISC 2019

(a) Acetaldehyde reacts with hydrogen cyanide.

(b) Acetone reacts with phenyl hydrazine.

Ans :

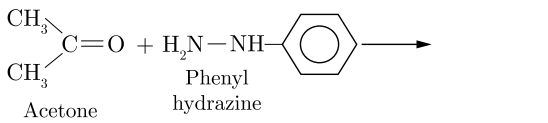
(a) Acetaldehyde reacts with hydrogen cyanide to give ethane cyanohydrin



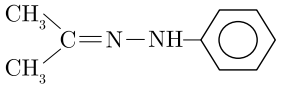
Acetaldehyde — Hydrogen cyanide — Ethane cyanohydrin

Above reaction is a nucleophilic addition reaction.

(b) Acetone reacts with phenyl hydrazine to give phenyl hydrazone.



Acetone — Phenyl hydrazine



Phenyl hydrazone

137. Write the balanced equations for the reaction of ammonia with formaldehyde, acetaldehyde and acetone.

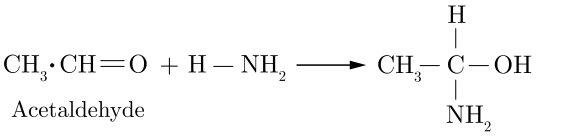
ISC 2001

Ans :

Ammonia with formaldehyde

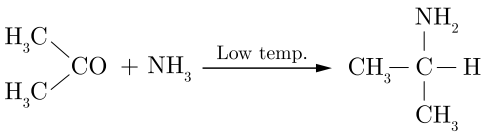
$\underset{\text{Formaldehyde}}{6HCHO} + 4NH_3 \longrightarrow 6H_2O + \underset{\substack{\text{Hexamethylene}\\\text{tetraamine}\\\text{(Urotropine)}}}{(CH_2)_6N_4}$

Ammonia with acetaldehyde

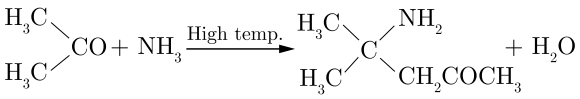


Acetaldehyde — Acetaldehyde ammonia

Ammonia with acetone



Acetone ammonia



Diacetone amine

138. Give balanced equations for the following reactions :

(i) Acetaldehyde is heated with hydroiodic acid in the presence of red phosphorus.

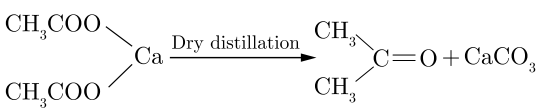
(ii) Calcium acetate is subjected to dry distillation.

(iii) Benzaldehyde is treated with sodium bisulphite.

ISC 2014

Ans :

(i) $\underset{\text{Acetaldehyde}}{CH_3CHO} + 4HI \xrightarrow[423\ K]{\text{Red P}} \underset{\text{Ethane}}{CH_3 - CH_3} + H_2O$

(ii) 

Calcium acetate — Acetone

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104. How will you convert methyl chloride into acetic acid?

ISC 2011

Ans :

The conversion of methyl chloride to acetic acid have the following steps

$$\underset{\text{Methyl chloride}}{CH_3Cl} + 2Na + Cl \cdot CH_3 \longrightarrow CH_3 \cdot CH_3 + 2NaCl$$

$$CH_3 \cdot CH_3 + Cl_2 \xrightarrow{h\nu} C_2H_5Cl + HCl$$

$$C_2H_5Cl + KOH(aq) \longrightarrow C_2H_5OH + KCl$$

$$C_2H_5OH + O_2 \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \underset{\text{Acetic acid}}{CH_3COOH} + H_2O$$

105. How will you distinguish between ethanol and acetic acid by a chemical test?

ISC 2018

Ans :

Ethanol and acetic acid : These can be distinguished by reaction with sodium bicarbonate.

Acetic acid reacts with sodium bicarbonate producing CO_2 gas, whereas ethanol does not show any reaction with sodium bicarbonate.

$$\underset{\text{Acetic acid}}{CH_3COOH} + NaHCO_3 \longrightarrow \underset{\text{Sodium acetate}}{CH_3COO^-Na^+} + \underset{\text{Effervescence}}{CO_2\uparrow} + H_2O$$

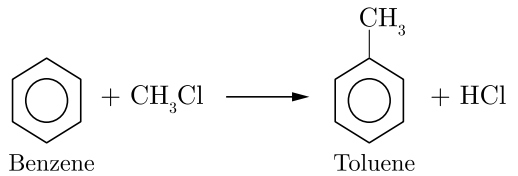
$$\underset{\text{Ethanol}}{CH_3CH_2OH} + NaHCO_3 \longrightarrow \text{No reaction}$$

106. How can benzene be converted into benzoic acid?

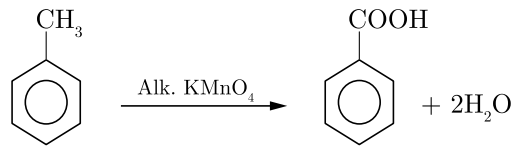
ISC 2011, 2007

Ans :

The conversion of benzene to benzoic acid have the following steps.



Benzene Toluene



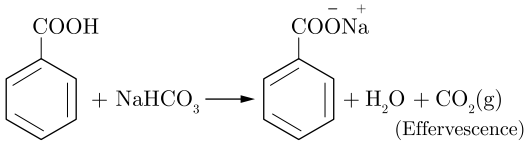
Toluene Benzoic acid

107. How will you distinguish between phenol and benzoic acid by a chemical test?

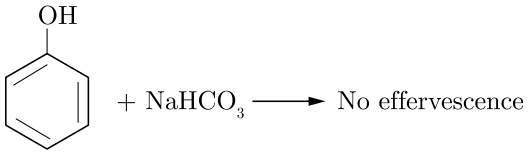
ISC 2019

Ans :

Phenol and benzoic acid can be distinguish by sodium bicarbonate test. Benzoic acid reacts with sodium bicarbonate to produce effervescence of carbon dioxide, whereas phenol does not.



Benzoic acid Sodium benzoate



Phenol

108. Give one test to distinguish between the following pair. Write the relevant equation.

Acetophenone and benzophenone

ISC 2014

Ans :

These can be distinguished by the iodoform test.

Acetophenone ($C_6H_5COCH_3$) due to the presence of

$CH_3\overset{\overset{O}{\|}}{C}-$ group gives yellow ppt. of iodoform on treatment with NaOI. While benzophenone ($C_6H_5COC_6H_5$) does not respond to this test.

$$C_6H_5COCH_3 + 3NaOI \longrightarrow \underset{\text{Sodium benzoate}}{C_6H_5COO^-Na^+} + \underset{\substack{\text{Iodoform}\\\text{(Yellow ppt.)}}}{CHI_3\downarrow} + 2NaOH$$

$$C_6H_5COC_6H_5 \xrightarrow{NaOI} \text{No yellow ppt. of } CHI_3$$

NODIA

121. Give one reason each for the following.

Acetone reacts with hydroxylamine to form only one product which has no geometrical isomer, but acetaldehyde reacts with hydroxylamine to form a product which has two geometrical isomers.

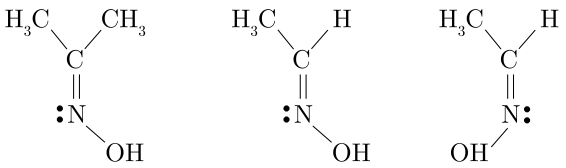
ISC 2007

Ans :

This is because when acetone reacts with $-NH_2OH$, acetoxime formed has two identical groups, $-CH_3$ attached to carbon with which N forms a double bond. This does not fulfill conditions for geometrical isomerism.

But when acetaldehyde reacts with NH_2OH, acetaldoxime is formed which has two different groups attached to C forming double bond with nitrogen.

Therefore, it exhibits geometrical isomerism.



Acetoxime *Syn*-form *Anti*-form

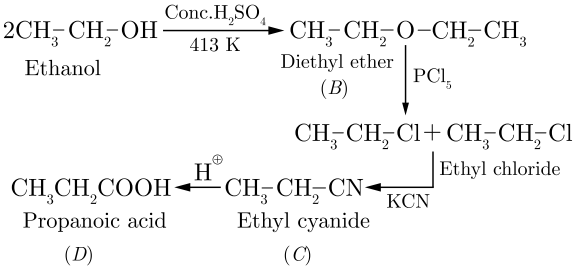
122. An organic compound $[A]$ C_2H_6O, on heating with conc. H_2SO_4 at 413 K gives a neutral compound $[B]C_4H_{10}O$. Compound $[B]$ on treatment with PCl_5 gives a product, which on subsequent treatment with KCN yields compound $[C]C_3H_5N$. Compound $[C]$ on hydrolysis gives an acid $[D]C_3H_6O_2$. Identify the compounds $[A]$, $[B]$, $[C]$ and $[D]$.

ISC 2023

Ans :

Organic compound having formula C_2H_6O is alcohol (CH_3CH_2OH) (A).

When ethyl alcohol is heated with conc. H_2SO_4 at 413 K it gives as ester $(C_4H_{10}O)$.



Ethanol Diethyl ether (B) Ethyl chloride Ethyl cyanide (C) Propanoic acid (D)

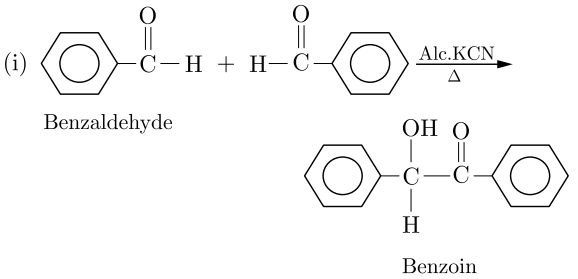
123. Write balanced chemical equations for the following and name the reactions occurring in each case :

(i) Benzaldehyde reacts with an alcoholic solution of potassium cyanide.

(ii) Propanone is treated with iodine and excess of alkali and warmed.

ISC 2006

Ans :

(i) 

Benzaldehyde Benzoin

This reaction is benzoin condensation.

(ii) $\underset{\text{Propanone}}{CH_3COCH_3} + 3I_2 + 4NaOH \xrightarrow{\Delta}$

$\underset{\text{Iodoform}}{CHI_3\downarrow} + CH_3\overset{-}{C}OO\overset{+}{N}a + 3NaI + 4H_2O$

This reaction is iodoform reaction.

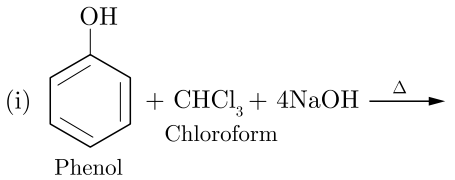
124. Give the balanced equations for the following reactions.

(i) Phenol heated with chloroform and sodium hydroxide.

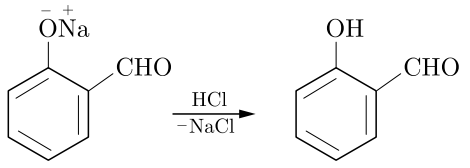
(ii) Acetaldehyde reacted with phenyl hydrazine.

ISC 2009

Ans :

(i) 

Phenol Chloroform



Sodium salt of salicylaldehyde (Major isomer) Salicyladehyde

(ii) $\underset{\text{Acetaldehyde}}{CH_3CHO} + \underset{\text{Phenyl hydrazine}}{H_2N \cdot NHC_6H_5} \longrightarrow$

$\underset{\text{Phenyl hydrazone}}{CH_3CH = N \cdot NHC_6H_5} + H_2O$

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Let us take an example

$$\underset{\text{Sodium acetate}}{2CH_3COO^-Na^+} \longrightarrow \underset{\text{Acetate ion}}{2CH_3COO^-} + 2Na^+$$

At anode,

$$\underset{\text{Acetate ion}}{2CH_3COO^-} \longrightarrow \underset{\text{Ethane}}{CH_3 - CH_3} + 2CO_2 + 2e^-$$

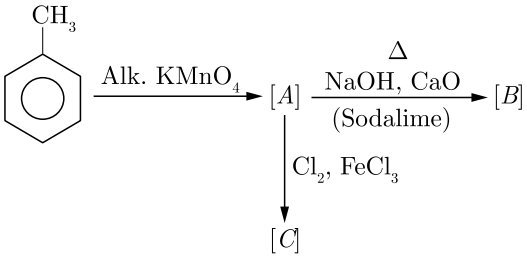
At cathode,

$$2H_2O \rightleftharpoons 2H^+ + 2OH^-$$

$$2H^+ + 2e^- \longrightarrow H_2$$

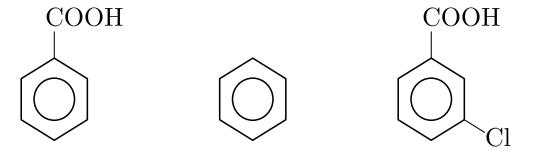
$$2Na^+ + 2OH^- \longrightarrow 2NaOH$$

117. Identify the products A, B and C.



Ans :

The products are



Benzoic acid (A) Benzene (B) m-chlorobenzoic acid (C)

118. Explain the following.

(a) Chloroacetic acid is stronger acid than acetic acid.

(b) Formic acid reduces Tollens' reagent but acetic acid does not.

ISC Specimen 2023

Ans :

(a) Cl-group in chloroacetic acid ($Cl - CH_2COOH$) is a electron withdrawing group. It increases the acidity of acetic acid by dispersing negative charge by inductive effect and stabilizing the acetate anion. Hence, chloroacetic acid is stronger acid than acetic acid.

(b) Formic acid is unique because it contain both aldehyde carboxylic group. Hence, it can act as reducing agent. It reduces Tollen's reagent. While acetic acid has no aldehyde group hence, it does not reduces Tollen's reagent.

119. Give one chemical test for each to distinguish between the following pairs of compound.

ISC 2021-22 (Sem-II)

(i) Acetaldehyde and benzaldehyde

(ii) Acetone and acetic acid

Ans :

(i) **Acetaldehyde and benzaldehyde** Fehling solution test is used to distinguish between acetaldehyde and benzaldehyde as benzaldehyde does not have α-hydrogen. Acetaldehyde gives red precipitate of cuprous oxide while benzaldehyde does not.

$$CH_3CHO + 5OH^- + 2Cu^{2+} \longrightarrow CH_3COO^- + \underset{\text{Red ppt.}}{Cu_2O\downarrow} + 3H_2O$$

(ii) **Acetone and acetic acid** Acetic acid on heating with ethyl alcohol in presence of H_2SO_4 gives a fruity smell of an ester, while acetone does not give this test.

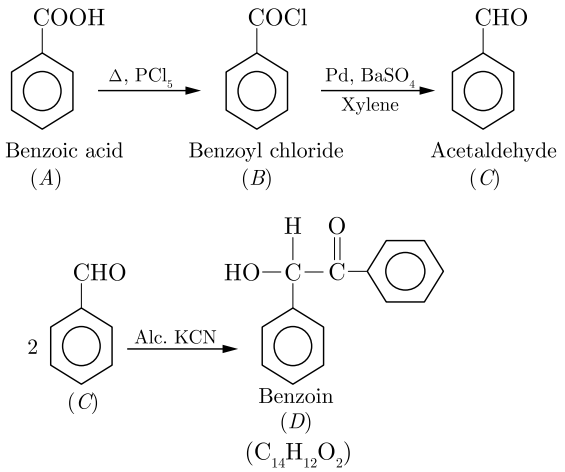
$$\underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Ethanol}}{C_2H_5OH} \xrightarrow[\text{Conc. } H_2SO_4]{\Delta} \underset{\text{Ester}}{CH_3COOC_2H_5} + H_2O$$

NODIA

120. An aromatic carboxylic acid $[A]$ which readily sublimes on heating produces compound $[B]$ on treatment with PCl_5. Compound $[B]$, when reduced in the presence of Pd catalyst over $BaSO_4$ poisoned by sulphur in xylene solution gives compound $[C]$.When compound $[C]$ is condensed in the presence of alcoholic KCN, it gives compound $[D]$. (Molecular formula of compound $[D]$ is $C_{14}H_{12}O_2$). Identify the compounds $[A]$, $[B]$, $[C]$ and $[D]$.

ISC 2023

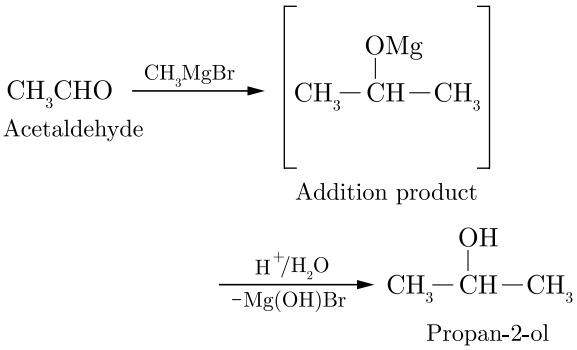
Ans :



98. How can the following conversion be brought about acetaldehyde to propan-2-ol?

ISC 2017

Ans :



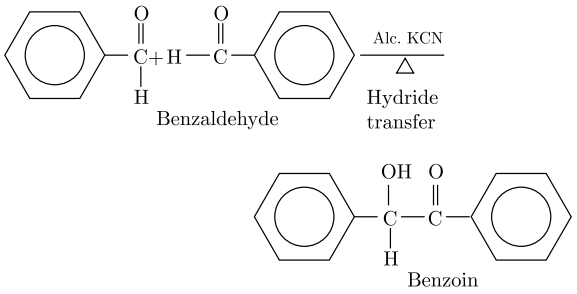
99. Give the balanced equation for the following name reaction.

Benzoin condensation

ISC 2016

Ans :

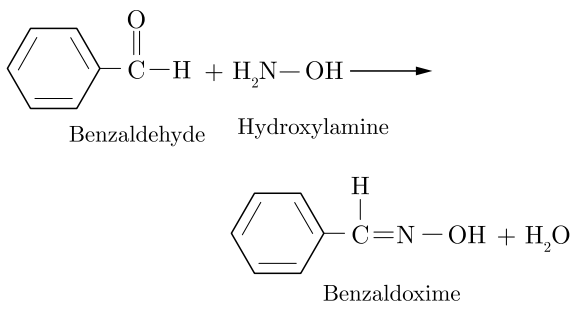
Benzoin condensation



100. Write the balanced chemical equation for the reaction between benzaldehyde and hydroxylamine.

ISC 2012

Ans :

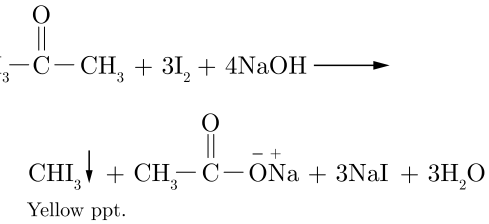


101. Explain the haloform reaction with one example.

ISC 2007

Ans :

Aldehydes and ketones having $CH_3-\overset{\overset{O}{\|}}{C}-$ group can be oxidised with sodium hypohalite $[NaOX]$ to give a haloform (CHX_3) and the salt of carboxylic acid. This reaction is called haloform reaction.

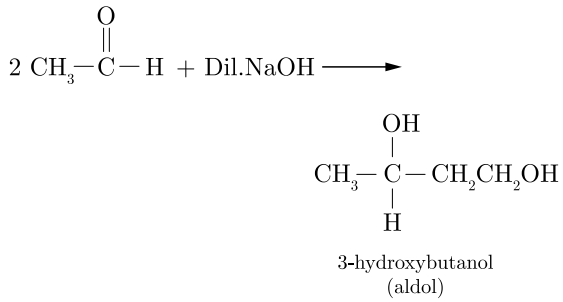


102. Name the following reaction and write balanced equation :

Acetaldehyde with dilute sodium hydroxide

ISC 2002

Ans :



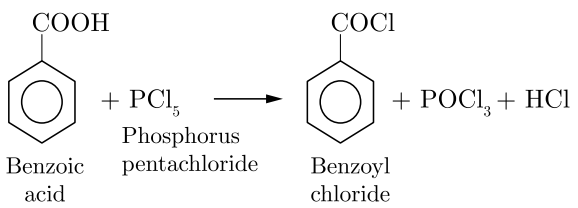
This reaction is called aldol condensation.

103. Write the balanced chemical equation for the reaction between benzoic acid and phosphorus pentachloride.

ISC 2012

Ans :

The balanced chemical equation is



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125. Give one chemical test for each to distinguish between the following pair of compounds.

ISC Specimen 2023

(i) Formaldehyde and acetic acid.

(ii) Acetaldehyde and acetone.

Ans :

(i) Formaldehyde and acetic acid Aldehyde reduces Tollen's reagent to give shining silver mirror but acetic acid does not.

$$\underset{\text{Formaldehyde}}{HCHO} + 2\underset{\text{Tollen's reagent}}{[Ag(NH_3)_2]^+} + 3OH^- \longrightarrow$$

$$HC(=O)O^- + 2Ag\downarrow + 2H_2O$$

Silver mirror

$$\underset{\text{Tollen's reagent}}{CH_3COOH} \longrightarrow \text{No reaction}$$

(ii) Acetaldehyde and acetone Acetaldehyde gives a silver mirror test with Tollen's reagent but acetone gives no such test with Tollen's reagent.

$$CH_3-C(=O)-H + 2[Ag(NH_3)_2]^+ \longrightarrow CH_3-C(=O)-O^- + 2Ag + H_2O$$

$$CH_3-C(=O)-CH_3 \xrightarrow{[Ag(NH_3)_2]^+} \text{No reaction}$$

126. How will you bring about the following conversions?(Give equation).

ISC Specimen 2021-22 (Sem-II)

(i) Acetic acid to acetone

(ii) Formaldehyde to urotropine

Ans :

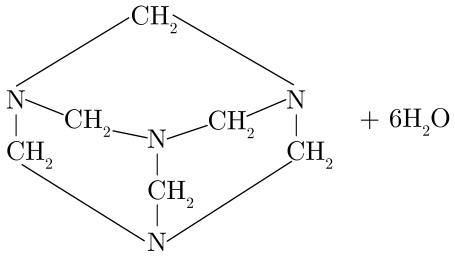
(i) Acetic acid to acetone

$$\underset{\text{Acetic acid}}{2\,CH_3COOH} \xrightarrow{Ca(OH)_2} \underset{\text{Calcium acetate}}{(CH_3COO)_2Ca^{2+}} \xrightarrow[\text{distillation}]{\text{Dry}} CH_3-C(=O)-CH_3 + CaCO_3$$

Acetone

(ii) Formaldehyde to urotropine

$$\underset{\text{Formaldehyde}}{6HCHO} + \underset{\text{Ammonia}}{4NH_3} \xrightarrow{50^\circ - 70^\circ C}$$



$+ 6H_2O$

Urotropine

127. Write chemical equations to illustrate each of the following name reactions.

ISC 2021-22 (Sem-II)

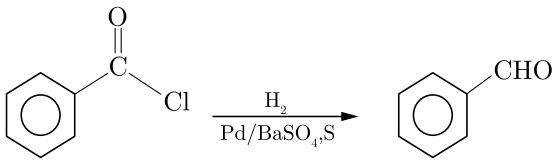
(i) Rosenmund reduction

(ii) Clemmensen reduction

Ans :

(i) **Rosenmund reduction :** Acyl chloride or acid chloride is hydrogenated in the presence of palladium catalyst supported over and partially poisoned by the addition of sulphur or barium sulphate. This reaction is called Rosenmund reduction.

$$\underset{\text{Acetyl chloride}}{CH_3-C(=O)-Cl} \xrightarrow[Pd/BaSO_4,S]{H} \underset{\text{Acetaldehyde}}{CH_3-C(=O)-H}$$



Benzoyl chloride Benzaldehyde

(ii) **Clemmensen reduction** It involves reduction of carbonyl group of an aldehyde or ketone to methylene group to form a hydrocarbon. Clemmensen reduction is carried out in presence of Zn amalgam and conc. HCl.

$$>C=O + 4[H] \xrightarrow{Zn\text{-}Hg/conc.HCl} >CH_2 + H_2O$$

Hydrocarbon

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128. Give the balanced equations for the following name reactions.

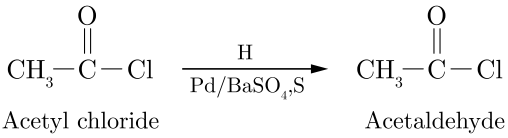
(i) Rosenmund reaction

(ii) Formaldehyde is treated with ammonia.

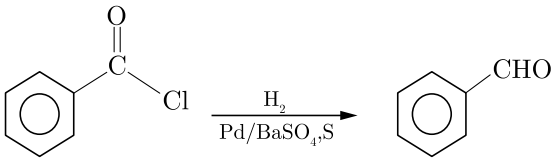
ISC 2015

Ans :

(i) **Rosenmund reduction :** Acyl chloride or acid chloride is hydrogenated in the presence of palladium catalyst supported over and partially poisoned by the addition of sulphur or barium sulphate. This reaction is called Rosenmund reduction.



Acetyl chloride — Acetaldehyde



Benzoyl chloride — Benzaldehyde

(ii) Formaldehyde reacts with ammonia to form hexamethylene tetraamine. Also, known as urotropine.

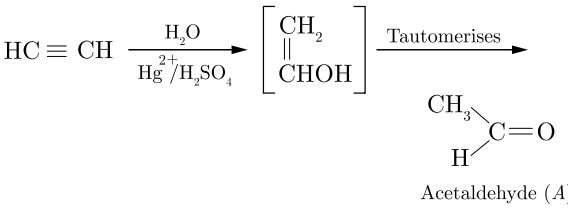
$$\underset{\text{Formaldehyde}}{6HCHO} + 4NH_3 \xrightarrow{\Delta} \underset{\substack{\text{(Urotropine)}\\ \text{Hexamethylenetetraamine}}}{(CH_2)_6N_4} + 6H_2O$$

129. Identify the compounds A, B, C and D in the given reaction.

$$HC \equiv CH \xrightarrow[Hg^{2+}/H_2SO_4]{H_2O} [A] \xrightarrow[K_2Cr_2O_7+H_2SO_4]{[O]} [B] \xrightarrow{Ca(OH)_2} [C] \xrightarrow[\text{Dry distillation}]{\text{Heat}} [D]$$

ISC 2019

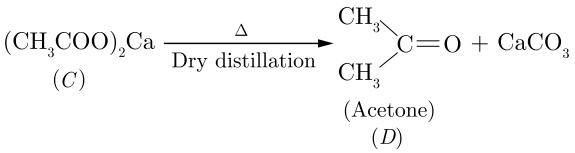
Ans :



Acetaldehyde (A)

$$\underset{(A)}{CH_3-CHO} \xrightarrow[K_2Cr_2O_7+H_2SO_4]{[O]} \underset{\substack{\text{(Acetic acid)}\\ (B)}}{CH_3COOH}$$

$$\underset{(B)}{CH_3COOH} \xrightarrow{Ca(OH)_2} \underset{(C)}{(CH_3COO)_2Ca}$$

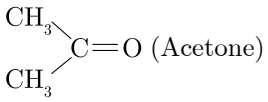


(Acetone) (D)

$(A) = CH_3 - CHO$ (Acetaldehyde)

$(B) = CH_3COOH$ (Acetic acid)

$(C) = (CH_3COO)_2Ca$ (Calcium acetate)

$(D) =$  (Acetone)

130. Give an example (equation) for each of the following name reactions.

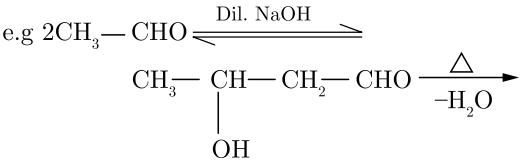
(i) Aldol condensation

(ii) Rosenmund reduction

ISC 2011, 2007

Ans :

(i) Aldehydes and ketones containing α-H atoms undergo aldol condensation in presence of dilute alkali as catalyst.

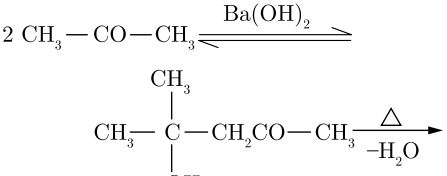


3-hydroxybutanal (aldol)

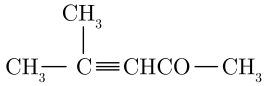
$CH_3-CH \equiv CH_2-CHO$

But-2-enal

(aldol condensation product)



4-hydroxy-4-methylpentan-2-one



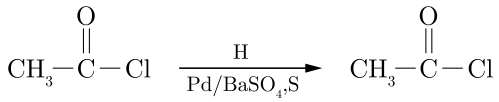
4-methylpent-3-en-2-one

(aldol condensation product)

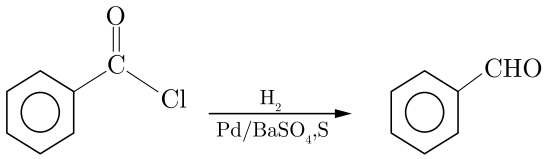
(mesityl oxide)

NODIA

(ii) **Rosenmund reduction :** Acyl chloride or acid chloride is hydrogenated in the presence of palladium catalyst supported over and partially poisoned by the addition of sulphur or barium sulphate. This reaction is called Rosenmund reduction.



Acetyl chloride Acetaldehyde



Benzoyl chloride Benzaldehyde

THREE MARKS QUESTIONS

131. Identify A to F.

$$[A] \xrightarrow{LiAlH_4} C_2H_5OH \xrightarrow{PBr_3} [B] \xrightarrow{KCN}$$

$$[C] \xrightarrow{D} C_3H_7NH_2 \xrightarrow{HNO_2} [E] \xrightarrow[K_2Cr_2O_7/H^+]{[O]} [F]$$

ISC 2011

Ans :

Substance from A to F are

A is acetic acid (CH_3COOH).

B is ethyl bromide (C_2H_5Br)

C is ethyl cyanide (C_2H_5CN).

D is H_2/Pt or $LiAlH_4$.

E is propyl alcohol (C_3H_7OH).

F is propionic acid (C_2H_5COOH).

132. What is Cannizzaro reaction? Name a compound which undergoes this reaction. Name the products formed when this compound undergoes the reaction.

ISC 2000

Ans :

Aldehydes which do not have α-hydrogen atom, when treated with concentrated solution of NaOH or KOH undergoes simultaneous oxidation and reaction forming salts of carboxylic acid and alcohol.

e.g. Formaldehyde undergoes Cannizzaro reaction to form product sodium formate and methyl alcohol.

The reaction can be represented as follows

$$\underset{\text{Formaldehyde}}{2HCHO} + \underset{\text{(Conc.)}}{NaOH} \longrightarrow \underset{\text{Sodium formate}}{HCOO^-Na^+} + \underset{\text{Methyl alcohol}}{CH_3OH}$$

133. Give balanced equations for the following reactions.

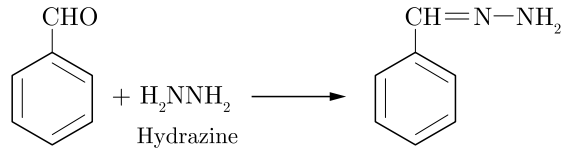
ISC 2018

(a) Benzaldehyde reacts with hydrazine.

(b) Acetone reacts with sodium bisulphite.

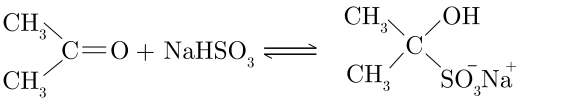
Ans :

(a) Benzaldehyde reacts with hydrazine



Benzaldehyde Benzaldehyde hydrazone

(b) Acetone reacts with sodium bisulphite



Acetone Acetone sodium bisulphite (addition product)

134. Write the product(s) of the following reactions.

(a) $CH_3COCH_3 + H_2NOH \longrightarrow$

(b) $2C_6H_5CHO + \text{Conc.}NaOH \longrightarrow$

(c) $CH_3COOH \xrightarrow{Cl_2/P}$

ISC Specimen 2018

Ans :

(a) $CH_3COCH_3 + H_2NOH \xrightarrow[-H_2O]{} (CH_3)_2C{=}NOH$

(b) $2\,C_6H_5CHO + \text{Conc. NaOH} \xrightarrow[\text{Cannizzaro reaction}]{\Delta}$

Benzaldehyde

$C_6H_5CH_2OH + C_6H_5COO^-Na^+$

Benzyl alcohol Sodium benzoate

(c) $CH_3COOH \xrightarrow[\text{HVZ reaction}]{Cl_2/P} \underset{\displaystyle Cl}{\overset{\displaystyle |}{CH_2}}{-}COOH$

α-chloroacetic acid

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TWO MARKS QUESTIONS

109. How will you convert the following ? (Give balanced equation).

ISC 2020

(i) Methyl chloride to acetic acid

(ii) Acetic acid to methane

Ans :

(i) $\underset{\text{Methylchloride}}{CH_3-Cl} \xrightarrow{Mg/Ether} CH_3MgCl \xrightarrow[(b)\ Water]{(a)\ CO_2} \underset{\text{Acetic acid}}{CH_3COOH}$

(ii) $\underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{NaOH} CH_3COO^-Na^+ \xrightarrow[\Delta]{NaOH/CaO} \underset{\text{Methane}}{CH_4}$

110. Write the structures of three compounds which have the same molecular formula of C_4H_8O but have different functional groups.

ISC 2006

Ans :

(i) Butanal $CH_3CH_2CH_2CHO$, (An aldehyde)

(ii) Butanone $CH_3COCH_2CH_3$, (A ketone)

(iii) An unsaturated alcohol, i.e. butanol
$CH_2 = CH - CH_2 - CH_2OH$

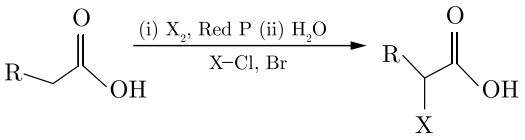
111. (i) Write the chemical equations to illustrate following name reactions. HVZ reaction.

(ii) How will the following the converted? (Give chemical equation)Acetic acid to methane

ISC 2021-22 (Sem-II)

Ans :

(i)



(ii) $\underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{NaOH} CH_3COO^-Na^+ \xrightarrow[\Delta]{NaOH/CaO} \underset{\text{Methane}}{CH_4}$

112. Give one chemical test to distinguish between acetaldehyde and benzaldehyde.

ISC 2018

Ans :

Acetaldehyde and benzaldehyde : Fehling solution test is used to distinguish between acetaldehyde and benzaldehyde as benzaldehyde does not have α-hydrogen.

Acetaldehyde gives red precipitate of cuprous oxide while benzaldehyde does not.

$$CH_3CHO + 5OH^- + 2Cu^{2+} \longrightarrow CH_3COO^- + \underset{\text{Red ppt.}}{Cu_2O\downarrow} + 3H_2O$$

113. How will the following be converted ?

(a) Acetaldehyde to acetone

(b) Formaldehyde to urotropine
(Give chemical equations)

ISC 2023

Ans :

(a) $\underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow[[O]]{K_2Cr_2O_7/H^+} \underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{Ca(OH)_2} (CH_3COO)_2Ca \xrightarrow{Heat} \underset{\text{Acetone}}{CH_3COCH_3}$

(b) Formaldehyde reacts with ammonia to form hexamethylene tetraamine (urotropine).

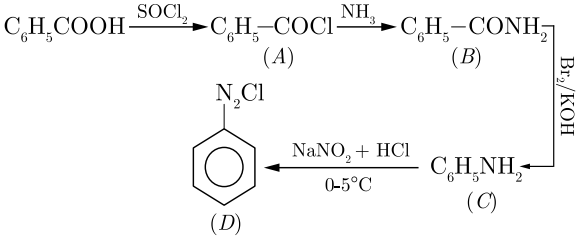
$$6HCHO + 4NH_3 \longrightarrow (CH_2)_6N_4 + 6H_2O$$

114. Identify the compounds A, B, C and D.

ISC 2020

$$C_6H_5COOH \xrightarrow{SOCl_2} [A] \xrightarrow{NH_3} [B] \xrightarrow{Br_2/KOH} [C] \xrightarrow[0.5^\circ C]{NaNO_2+HCl} [D]$$

Ans :



115. Correct the following statements by changing the underlined part of the sentence. (Do not change the whole sentence)

(i) Acetone gives a white precipitate on <u>treatment with sodium chloride</u>.

(ii) Acetaldehyde undergoes <u>Cannizzaro reaction</u> on treatment with dilute alkali.

ISC 2008

Ans :

(i) Acetone gives a white precipitate on treatment with sodium bisulphate.

(ii) Acetaldehyde undergoes aldol condensation on treatment with dilute alkali.

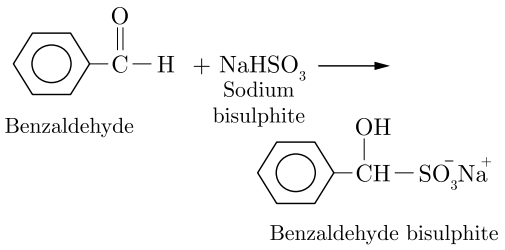
116. Give the balanced equations for the following reaction: Kolbe's electrolytic reaction

ISC 2014

Ans :

Kolbe's electrolytic reaction can be proceed as follows

NODIA

(iii) 

139. Write chemical equations to illustrate the following name reactions.

ISC 2018

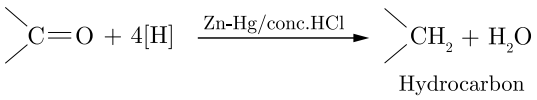
(a) Clemmensen reduction

(b) Rosenmund reduction

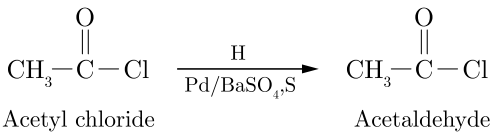
Ans :

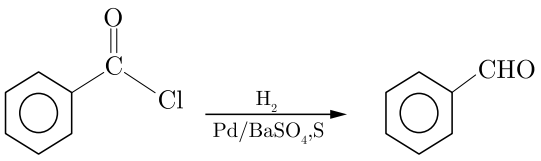
(a) **Clemmensen reduction** It involves reduction of carbonyl group of an aldehyde or ketone to methylene group to form a hydrocarbon.

Clemmensen reduction is carried out in presence of Zn amalgam and conc. HCl.



(b) **Rosenmund reduction** Acyl chloride or acid chloride is hydrogenated in the presence of palladium catalyst supported over and partially poisoned by the addition of sulphur or barium sulphate. This reaction is called Rosenmund reduction.





140. How can the following conversions be brought about ?

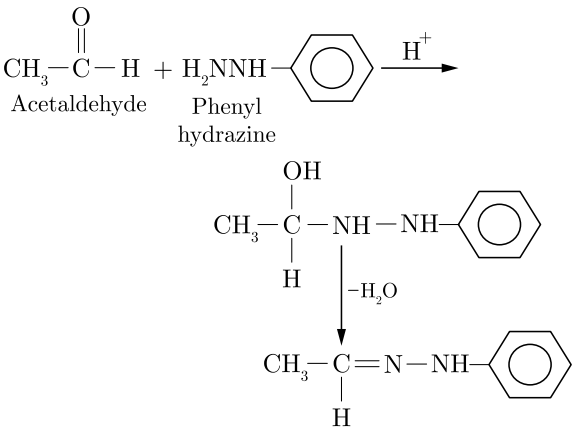
(i) Acetaldehyde to acetaldehyde phenyl hydrazone.

(ii) Methyl chloride to acetone.

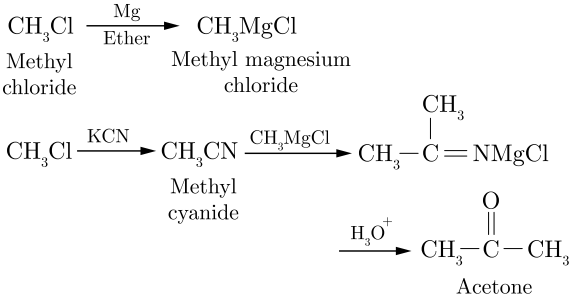
ISC 2016

Ans :

(i) Acetaldehyde reacts with phenyl hydrazine in acidic medium to form an addition compound, which undergoes elimination of a water molecule to form acetaldehyde phenyl hydrazone.



(ii)



141. A ketone $A(C_4H_8O)$ which undergoes iodoform reaction gives compound B on reduction. B on heating with conc. H_2SO_4 at 443 K gives a compound C which forms ozonide D. D on hydrolysis with Zn dust gives only E. Identify the compounds A to E. Write the iodoform reaction with compound A.

ISC 2020

Ans :

The road map of the given equation is as follows The only possible ketone formed from the given formula which gives iodoform reaction is

2-butanone i.e. $CH_3CH_2-\overset{\overset{O}{\|}}{C}-CH_3$. This is compound A.

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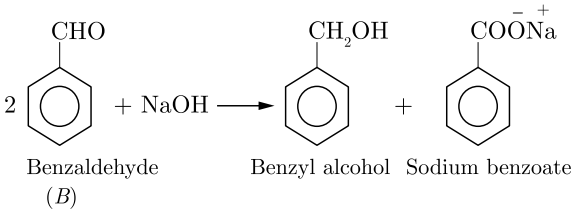
(ii) When benzaldehyde reacts with sodium hydroxide then the benzyl alcohol and sodium benzoate are formed. This reaction is knows as Cannizzaro reaction.



Benzaldehyde (B) | Benzyl alcohol | Sodium benzoate

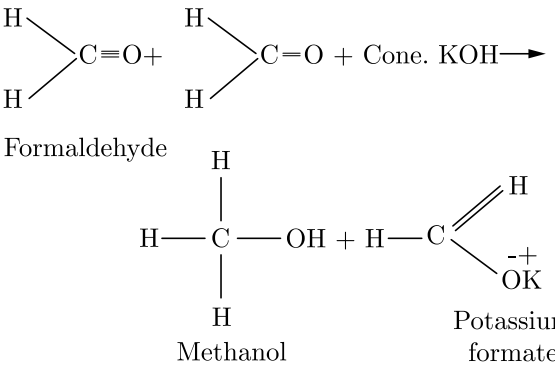
151. Write the chemical equations to illustrate the following name reactions. ISC 2023

(a) Cannizzaro reaction
(b) HVZ reaction
(c) Aldol condensation

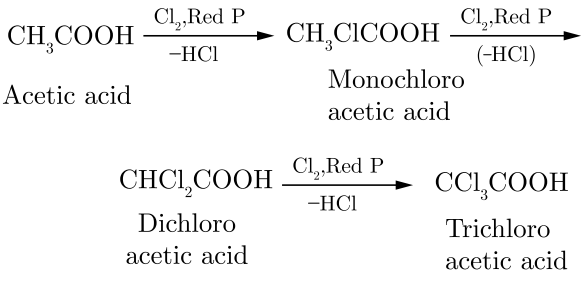
Ans :

(a) Cannizzaro reaction : Aldehydes which do not have α-H atoms undergo self oxidation and reduction (dispropodionation) on treatment with conc. alkali.

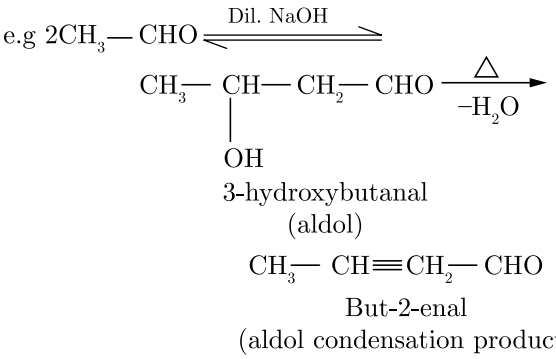
In this reaction, one molecule ofaldehyde is reduced to alcohol while another molecule is oxidised to salt of carboxylic acid.

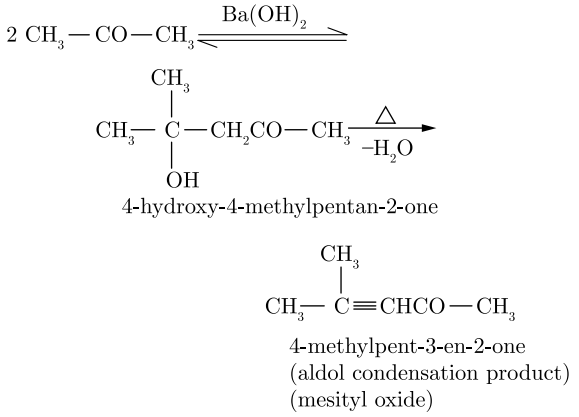


(b) HVZ reaction



(c) Aldol condensation



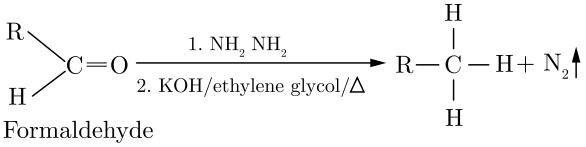


152. Write the chemical equations to illustrate the following name reactions. ISC Specimen 2018

(a) Wolff-Kishner reduction
(b) Aldol condensation
(c) Cannizzaro reaction

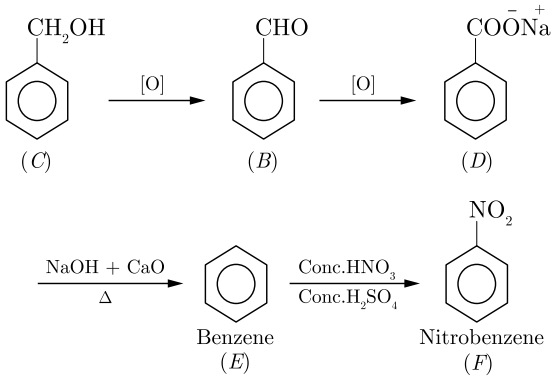
Ans :

(a) Wolff-Kishner reduction : Reduction of carbonyl compounds into hydrocarbon The carbonyl group of aldehydes and ketones is reduced to CH_2 group (hydrocarbons) on treatment with hydrazine followed by heating with sodium or potassium hydroxide in high boiling solvent such as ethylene glycol is known as Wolff-Kishner reduction.



Formaldehyde

NODIA



Therefore, E is benzene and F is nitrobenzene.

144. Write the balanced chemical equation for the following reaction.

(i) Oxalic acid is treated with acidified potassium permanganate solution.

(ii) Benzoic acid is treated with a mixture of concentrated nitric acid and concentrated sulphuric acid.

(iii) Methyl magnesium iodide is treated with carbon dioxide and the product hydrolysed in acidic medium.

ISC 2013

Ans :

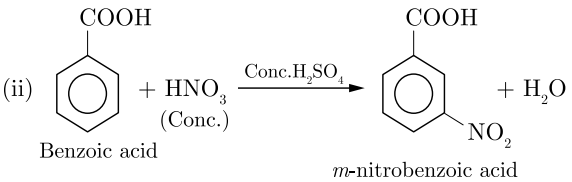
The balanced chemical equations for the given reactions are as follows

(i) $5\begin{pmatrix}COOH\\|\\COOH\end{pmatrix} + 2KMnO_4 + 3H_2SO_4 \longrightarrow$

Oxalic acid; Potassium permanganate

$K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$

(Colourless)

(ii) 

(iii) $O{=}C{=}O + CH_3{-}Mg{-}I \longrightarrow O{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}OMgI$

Carbon dioxide; Methyl magnesium iodide

$\xrightarrow{H_2O/H^+} CH_3{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}OH + Mg\begin{matrix}OH\\I\end{matrix}$

Acetic acid; Hydroxy magnesium iodide

145. Write the chemical equation for the following named organic reactions.

ISC Specimen 2023

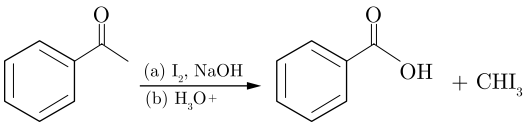
(i) Haloform reaction

(ii) Reimer - Tiemann reaction

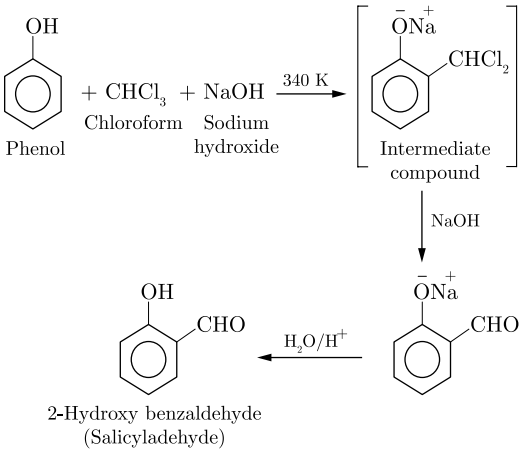
(iii) Kolbe - Schmidt reaction or Kolbe reaction

Ans :

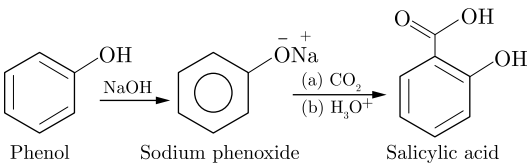
(i) Haloform reaction is reaction of methyl ketone with chlorine, bromine, or iodine in the presence of hydroxide ions to give a carboxylate ion and a haloform. The formed carboxylate ion on hydrolysis gives benzoic acid.



(ii) Reimer-Tiemann reaction is an organic chemical reaction where phenol is converted into an *ortho*-hydroxy benzaldehyde using chloroform, a base and acid workup.



(iii) **Kolbe-Schmidt reaction or Kolbe reaction :** When phenol is treated with sodium hydroxide, sodium phenoxide is produced. This sodium phenoxide when treated with carbon dioxide, followed by acidification undergoes electrophilic substitution to give *ortho*-hydroxy benzoic acid as the main product.



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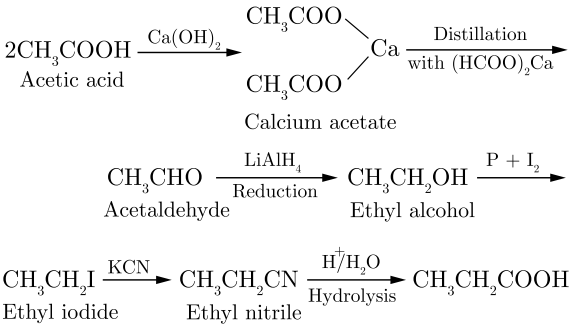
FOUR MARKS QUESTIONS

146. How can acetic acid be converted into propionic acid?

ISC 2002

Ans :



147. An aliphatic unsaturated hydrocarbon $[A]$ when treated with $HgSO_4/H_2SO_4$ yields a compound $[B]$ having molecular formula C_3H_6O. $[B]$ on oxidation with concentrated HNO_3 gives two compounds $[C]$ and $[D]$. Compound $[C]$ when treated with PCl_5 gives compound $[E]$. $[E]$ when reacts with ethanol gives a sweet smelling liquid $[F]$. Compound $[F]$ is also formed when $[C]$ reacts with ethanol in the presence of concentrated H_2SO_4 .

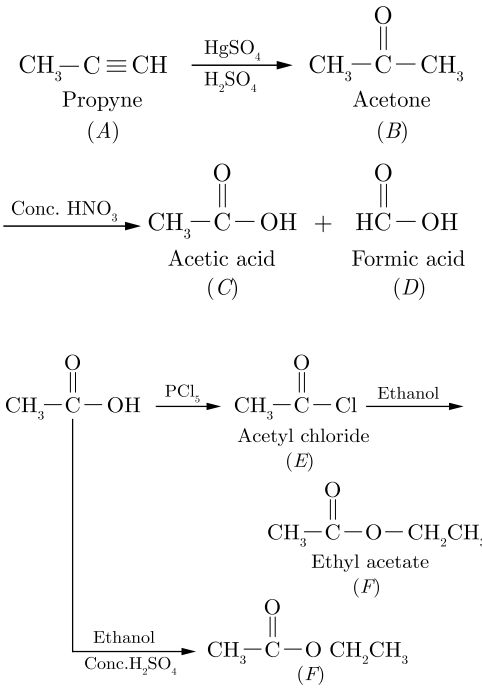
(i) Identify the compound A, B, C, D, E and F.

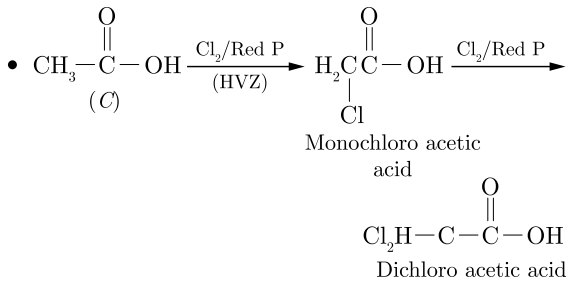
(ii) Give the chemical equation for the reaction of (C) with chlorine in the presence of red phosphorus and name the reaction.

ISC 2017

Ans :

The reaction takes place as follows





148. Starting with methyl magnesium bromide, how will the following compounds be synthesised?

ISC Specimen 2023

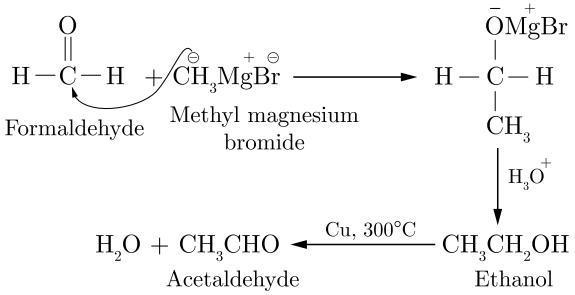
(a) Acetaldehyde

(b) Acetone

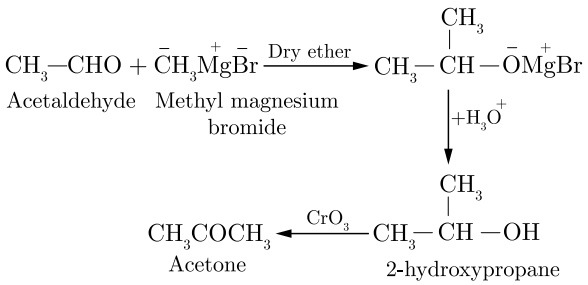
(c) Acetic acid

Ans :

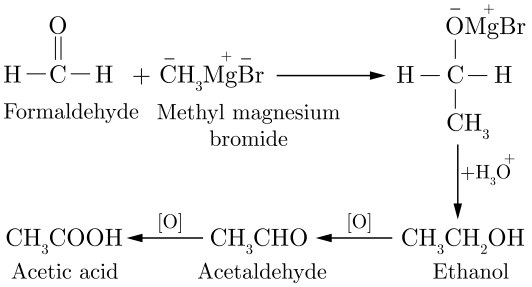
(a) Methyl magnesium bromide to ethanol



(b) Methyl magnesium bromide to acetone



(c) Methyl magnesium bromide to acetic acid



NODIA

149. Account for the following.

(a) CH_3CHO is more reactive with HCN than CH_3COCH_3.

(b) Carboxylic acids are stronger acids than phenol.

ISC Specimen 2018

Ans :

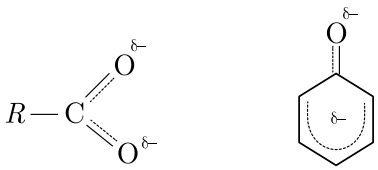
(a) CH_3CHO (aldehyde) is more reactive with HCN than CH_3COCH_3 (ketone) towards nucleophilic addition reactions. It can be explain by the following facts:

Inductive effect : Since, an alkyl group has electron donating $(+I)$ inductive effect. Hence, greater the number of alkyl groups attached to carbonyl group, greater the electron density on carbonyl carbon. Thus, it lowers the attack of nucleophile and hence, reactivity decreases. Hence,

Aldehyde Ketone

Steric effect : As the number of alkyl group attached to carbonyl carbon increases, the attack of nucleophil on carbonyl group becomes more and more difficult due to steric hindrance. Therefore, due to the presence of two bulky alkyl (or R) groups, the attack of nucleophile is hindered and hence ketones are less reactive than aldehydes

(b) Phenoxide ion has non-equivalent resonance structures in which the negative charge is less effectively delocalised overless electronegative carbon atom and one oxygen atom. While in carboxylate ion, the negative charge is delocalised over two electronegative oxygen atoms. Thus, carboxylate ion is much more resonance stabilised than phenoxide ion. Since, more stable the conjugate base of an acid, stronger is the acid.



Carboxylate ion Phenoxide ion

150. An organic compound A has the molecular formula C_7H_6O. When A is treated with NaOH followed by acid hydrolysis, it gives two products, B and C. When B is oxidised, it gives A. When A and C are each treated separately with PCl_3, they give two different organic products D and E.

(i) Identify A to E.

(ii) Give the chemical reaction when A is treated with NaOH and name the reaction.

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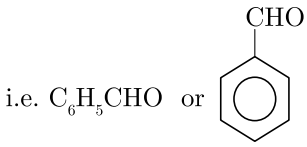
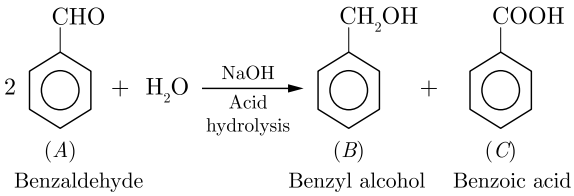
Ans :

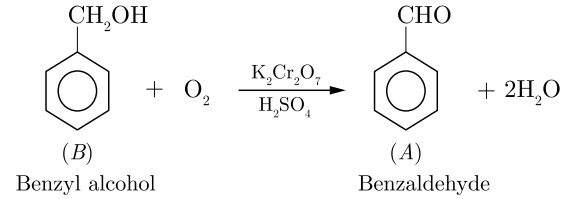
(i) The organic compound A, C_7H_6O is benzaldehyde.



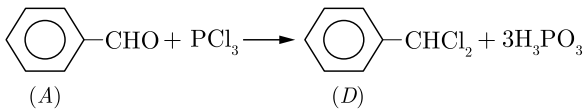
i.e. C_6H_5CHO or



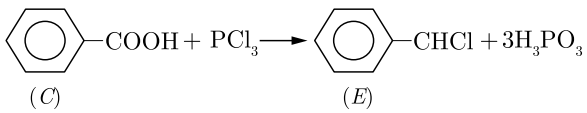
Benzaldehyde Benzyl alcohol Benzoic acid



Benzyl alcohol Benzaldehyde



Benzaldehyde Benzal chloride



Benzic acid Benzoyl chloride

Thus, A is benzaldehyde

B is benzyl alcohol.

C is benzoic acid.

D is benzal chloride.

E is benzoyl chloride.

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weaker acids and therefore cannot displace carbonic acid from sodium bicarbonate solution under ordinary conditions.

155. During an organic synthesis experiment, benzene was treated with carbon monoxide and hydrogen chloride in the presence of anhydrous aluminium chloride and cuprous chloride catalysts. An aromatic aldehyde was obtained as the product.
(i) Name the reaction involved in the process.
(ii) Which aromatic aldehyde is formed from benzene?
(iii) State the role of anhydrous aluminium chloride in the reaction.

Ans :
(i) Gattermann-Koch reaction.
(ii) Benzaldehyde.
(iii) Anhydrous aluminium chloride acts as Lewis acid catalyst and helps generate the electrophile required for electrophilic substitution. The electrophile attacks the benzene ring introducing the formyl group and producing aromatic aldehyde.

156. A chemist dissolved benzoic acid in benzene and observed that the compound existed mainly as dimers instead of individual molecules. The teacher explained that intermolecular forces strongly influence the physical properties of carboxylic acids.
(i) Which intermolecular force causes dimer formation in carboxylic acids?
(ii) In which type of solvent is dimerisation commonly observed?
(iii) Explain how dimer formation affects the boiling point of carboxylic acids.

Ans :
(i) Hydrogen bonding.
(ii) Non-polar solvents.
(iii) Two carboxylic acid molecules associate through intermolecular hydrogen bonding forming cyclic dimers. Dimer formation increases molecular size and intermolecular attraction. Consequently larger amount of energy is required to separate molecules during boiling, leading to unusually high boiling points of carboxylic acids.

157. A student performed Tollens' test on two carbonyl compounds, ethanal and propanone. Ethanal produced a bright silver mirror on the inner walls of the test tube whereas propanone did not show any visible reaction. The teacher explained that aldehydes are easily oxidised under mild conditions while ketones generally resist oxidation because of structural differences around the carbonyl carbon.
(i) Which compound gave positive Tollens' test?
(ii) What is the visible observation in Tollens' test?
(iii) Why do aldehydes react more readily with Tollens' reagent than ketones?

Ans :
(i) Ethanal.
(ii) Formation of silver mirror.
(iii) Aldehydes contain hydrogen atom directly attached to carbonyl carbon and therefore undergo oxidation easily. Tollens' reagent oxidises aldehydes into carboxylic acids while silver ions are reduced to metallic silver. Ketones lack such hydrogen atom and hence generally resist oxidation under mild conditions.

158. A chemist treated benzaldehyde with concentrated sodium hydroxide solution. After completion of the reaction, benzyl alcohol and sodium benzoate were obtained as products. The teacher explained that this reaction is characteristic of aldehydes lacking alpha hydrogen atoms.
(i) Name the reaction involved in the above process.
(ii) Why does benzaldehyde undergo this reaction?
(iii) Write the products formed during the reaction.

Ans :
(i) Cannizzaro reaction.
(ii) Benzaldehyde lacks alpha hydrogen atom.
(iii) $2C_6H_5CHO + NaOH \rightarrow C_6H_5CH_2OH + C_6H_5COONa$
One molecule of benzaldehyde undergoes oxidation to sodium benzoate while another molecule undergoes reduction to benzyl alcohol.

159. A student compared the reactivity of formaldehyde and acetone towards nucleophilic addition reactions. Formaldehyde reacted rapidly while acetone reacted comparatively slowly. The teacher explained that both steric factors and inductive effects influence the reactivity of carbonyl compounds.
(i) Which compound reacted faster towards nucleophilic addition?

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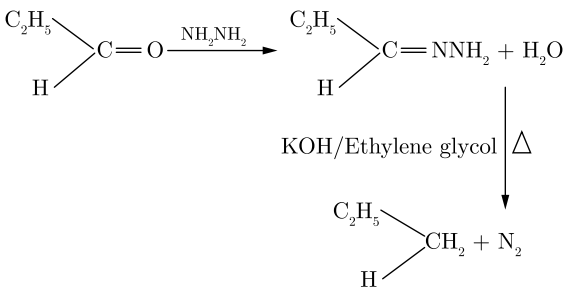
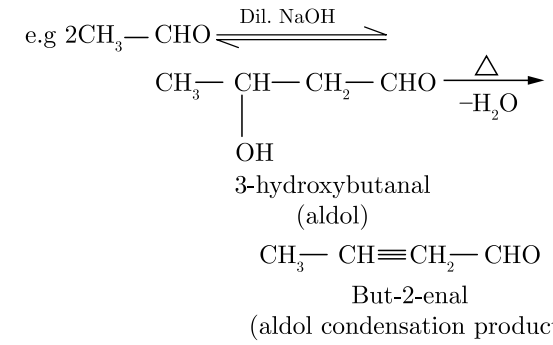
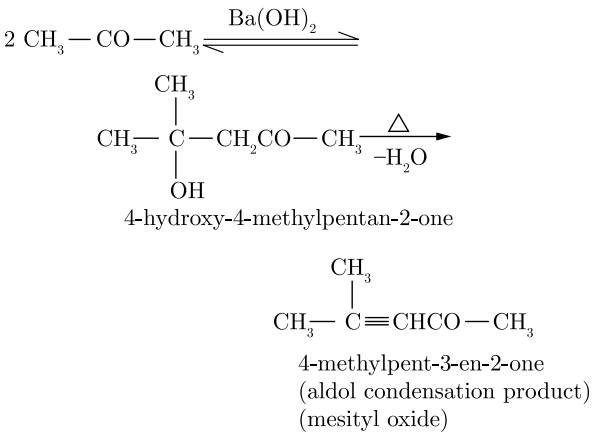
Mechanism of simple Wolff-kishner reductions are given below :

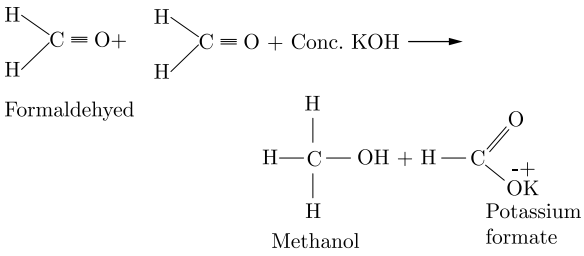


(b) Aldol condensation : Aldehydes and ketones containing α-H atoms undergo aldol condensation in presence of dilute alkali as catalyst.





(c) Cannizzaro reaction : Aldehydes which do not have a-H atoms undergo self oxidation and reduction (disproportionation) on treatment with conc. alkali.
In this reaction, one molecule of aldehyde is reduced to alcohol while another molecule is oxidised to salt of carboxylic acid.



CASE BASED QUESTIONS

153. A student compared the acidity of acetic acid, chloroacetic acid and trichloroacetic acid. It was observed that acidity increased significantly with increase in the number of chlorine atoms attached near the carboxyl group.

(i) Which acid among the three is strongest?
(ii) Which effect is responsible for increased acidity?
(iii) Explain why chlorine substitution increases acidic strength.

Ans :
(i) Trichloroacetic acid.
(ii) Negative inductive effect.
(iii) Chlorine atoms withdraw electron density through negative inductive effect stabilising the carboxylate ion formed after proton loss. Greater the stabilisation of conjugate base, stronger becomes the acid. Therefore acidity increases with increase in number of chlorine substituents.

154. A student added sodium bicarbonate solution separately to ethanol, phenol and acetic acid. Only one compound produced brisk effervescence with evolution of gas. The teacher explained that this test is commonly used to identify carboxylic acids.

(i) Which compound reacted with sodium bicarbonate?
(ii) Name the gas evolved during the reaction.
(iii) Why do alcohols and phenols not show similar reaction?

Ans :
(i) Acetic acid.
(ii) Carbon dioxide.
(iii) Carboxylic acids are sufficiently acidic to react with sodium bicarbonate producing carbon dioxide gas. Alcohols and phenols are much

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CHAPTER 9

Organic Compounds Containing Nitrogen

SUMMARY

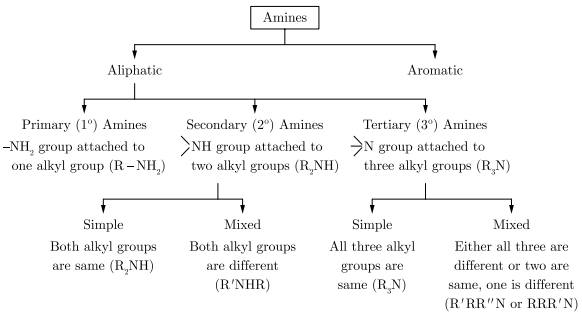
1. AMINES

These are alkyl or aryl derivatives of ammonia and are obtained by replacing one, two or three hydrogen atoms by alkyl/aryl groups.

1.1 Nomenclature

In common system, an aliphatic amine is named by prefixing alkyl group to amine, i.e., alkylamine. In IUPAC system, amines are names as alkanamines. In secondary and tertiary amines, when two or more groups are the same, the prefix di or tri is appended before the name of alkyl group.

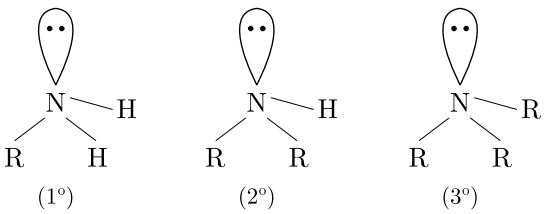
Classification :


Amines
Aliphatic
Aromatic
Primary (1°) Amines
–NH2 group attached to one alkyl group (R – NH2)
Secondary (2°) Amines
>NH group attached to two alkyl groups (R2NH)
Tertiary (3°) Amines
>N group attached to three alkyl groups (R3N)
Simple
Both alkyl groups are same (R2NH)
Mixed
Both alkyl groups are different (R′NHR)
Simple
All three alkyl groups are same (R3N)
Mixed
Either all three are different or two are same, one is different (R′RR″N or RRR′N)

1.2 Structure

Nitrogen orbitals in amines are sp^3- hybridised and the geometry of amines is pyramidal. Due to the presence of unshared pair of electrons, the angle $C-N-E$, (Where, E is C or H) is less than 109.5°.

Amines have trigonal pyramidal shapes in which N atom undergoes sp^3 hybridisation as :



1.3 General methods for the preparation of amines

(i) **From alkyl halides (Hofmann's ammonolysis) (Name Reaction) :**

$$CH_3Cl + NH_3 \xrightarrow{\text{Alcohol,373 K}} CH_3NH_2 + HCl$$

$$CH_3Cl + NH_3 \xrightarrow{\text{Alcohol, 373 K}} CH_3NH_2 + HCl$$

$$CH_3NH_2 + CH_3Cl \xrightarrow{\text{Alcohol, 373 K}} (CH_3)_2NH + HCl$$

$$(CH_3)_2NH + CH_3Cl \xrightarrow{\text{Alcohol, 373 K}} (CH_3)_3N + HCl$$

$$(CH_3)_3N + CH_3Cl \xrightarrow{\text{Alcohol, 373 K}} [(CH_3)_4N)^+ Cl^-$$

(ii) **From nitro compounds (By reduction) :**

$$RNO_2 + 6[H] \xrightarrow{\text{Sn + conc. HCl}} RNH_2 + 2H_2O$$

(iii) **From cyanides/isocyanides (By reduction) :**

$$CH_3CN + 4[H] \xrightarrow[\text{Ether}]{LiAlH_4} CH_3CH_2NH_2$$

Ethylamine

$$CH_3NC + 4[H] \xrightarrow[\text{Ether}]{LiAlH_4} (CH_3)_2NH$$

Dimethylamine

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(ii) Which effect decreases the reactivity of ketones?
(iii) Explain why formaldehyde is more reactive than acetone.

Ans :
(i) Formaldehyde.
(ii) Positive inductive effect of alkyl groups.
(iii) Formaldehyde does not contain electron donating alkyl groups and experiences minimum steric hindrance. Therefore the carbonyl carbon remains highly electrophilic. Acetone contains two alkyl groups which reduce positive character on carbonyl carbon and hinder nucleophilic attack, making it less reactive.

160. A laboratory assistant heated sodium acetate with soda lime during an organic preparation experiment. A gaseous hydrocarbon was evolved which burned with a pale blue flame. The chemistry teacher explained that the reaction involved removal of carbon dioxide from the carboxylate group.
(i) Name the reaction taking place in the experiment.
(ii) Which hydrocarbon is produced in the reaction?
(iii) Write the balanced chemical equation for the reaction.

Ans :
(i) Decarboxylation reaction.
(ii) Methane.
(iii) $CH_3COONa + NaOH \xrightarrow[\Delta]{CaO} CH_4 + Na_2CO_3$
During the reaction, one carbon atom is removed from the sodium salt of carboxylic acid in the form of carbon dioxide.

161. A student treated acetaldehyde with dilute sodium hydroxide solution and observed formation of a beta-hydroxy aldehyde. On heating, the product lost water and formed an unsaturated aldehyde. The teacher explained that aldehydes containing alpha hydrogen atoms undergo characteristic condensation reactions.
(i) Name the reaction involved in the above process.
(ii) Why does acetaldehyde undergo this reaction?
(iii) Name the final unsaturated product formed after dehydration.

Ans :
(i) Aldol condensation.
(ii) Acetaldehyde contains alpha hydrogen atoms.
(iii) Crotonaldehyde.
Initially beta-hydroxy aldehyde called aldol is formed which on heating loses water producing crotonaldehyde containing carbon-carbon double bond.

162. A chemist reduced propanone using hydrogen gas in the presence of platinum catalyst. After the reaction, a secondary alcohol was obtained. The teacher explained that catalytic hydrogenation converts carbonyl compounds into alcohols by addition of hydrogen across the carbonyl bond.
(i) Which alcohol is formed from propanone?
(ii) Which catalyst is commonly used in catalytic hydrogenation?
(iii) Explain why ketones produce secondary alcohols on reduction.

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Ans :
(i) Propan-2-ol.
(ii) Platinum catalyst.
(iii) In ketones, the carbonyl carbon is attached to two alkyl groups. Reduction converts the carbonyl group into hydroxyl group without changing the carbon skeleton. Since the hydroxyl-bearing carbon remains attached to two alkyl groups, secondary alcohols are formed.

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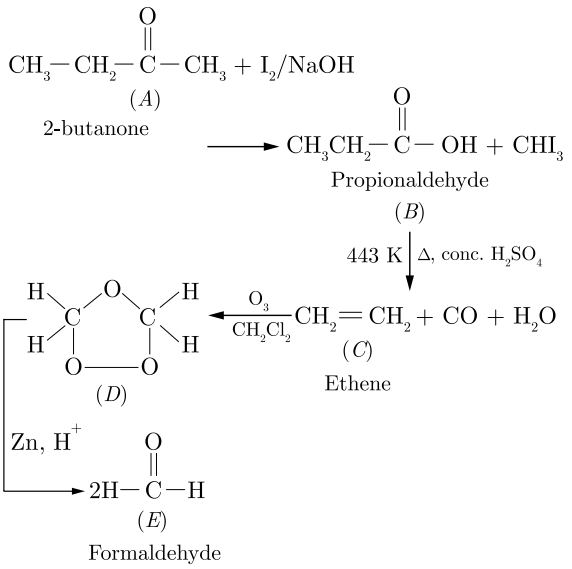
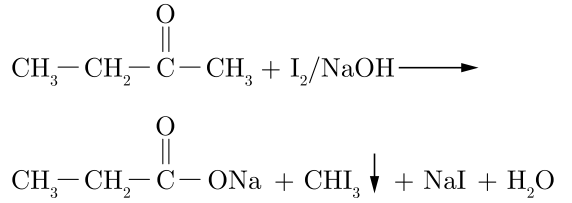


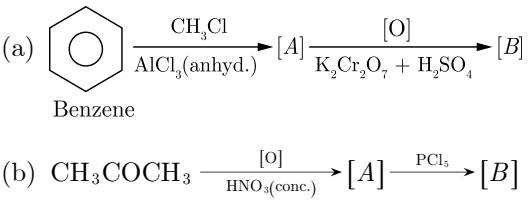
Iodoform reaction with compound A is as follows



142. (i) Write chemical equations to illustrate the following name reaction.
Cannizzaro reaction

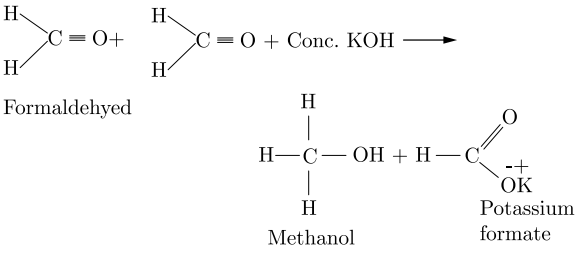
ISC 2019

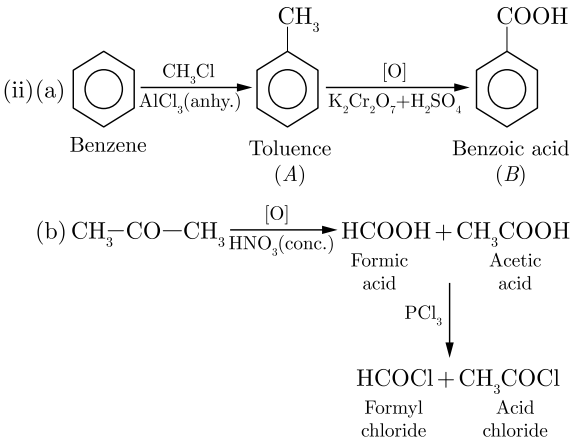
(ii) Identify the compounds A and B in the given reactions.



Ans :

(i) Cannizzaro reaction





If A is formic acid then B is formyl chloride. While if A is acetic acid then B is acid chloride.

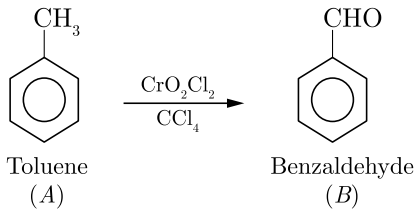
143. An organic compound A with molecular formula C_7H_8 on oxidation by chromylchloride in the presence of CCl_4 gives a compound B which gives positive Tollen's test. The compound B on treatment with NaOH followed by acid hydrolysis gives two products C and D. C on oxidation gives B which on further oxidation gives D.

The compound D on distillation with soda lime gives a hydrocarbon E. Below 60°C, concentrated nitric acid reacts with E in the presence of concentrated sulphuric acid forming a compound F. Identify the compounds A, B, C, D, E and F.

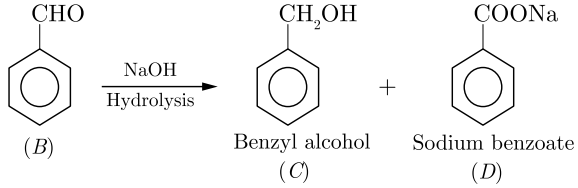
ISC 2014

Ans :

Compound A must be toluene and B should be benzaldehyde (as it gives positive Tollen's test).



Compound $B\,(C_6H_5CHO)$ on treatment with NaOH followed by acid hydrolysis gives two products, benzyl alcohol (C), and sodium benzoate (D). This is Cannizzaro reaction.



Compound C on oxidation gives B, which on further oxidation gives D, i.e.

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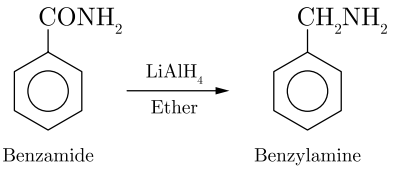
(iv) **From amides (By reduction) :**

$$CH_3CONH_2 + 4[H] \xrightarrow[EEt]{LiAlH_4} CH_3CH_2NH_2 + H_2O$$



(v) **Hofmann degradation method (Name Reaction) :**

$$CH_3CONH_2 + Br_2 + \underset{(aq)}{4KOH} \xrightarrow{\Delta} CH_3NH_2 + 2KBr + K_2CO_3 + 2H_2O$$

(vi) **From oximes (Be reduction) :**

$$\underset{\text{Aldoxime}}{RCH=NOH(aq)} + 4[H] \xrightarrow{LiAlH_4} \underset{(1^\circ\text{amine})}{RCH_2NH_2} + H_2O$$

(vii) **From aldehydes and ketons (Reductive amination) (Name Reaction) :**

$$RCHO + NH_3 \xrightarrow[-H_2O]{\Delta} RCH=NH \xrightarrow[Ni]{H_2} RCH_2NH_2$$

$$RCOR' + NH_3 \xrightarrow[-H_2O]{\Delta} \begin{matrix} R \\ R' \end{matrix}\!\!>\!C=NH \xrightarrow[Ni]{H_2} \begin{matrix} R \\ R' \end{matrix}\!\!>\!CHNH_2$$

(viii) **From alcohols :**

$$CH_3CH_2OH + NH_3 \xrightarrow[523\,K]{Al_2O_3} \underset{(1^\circ\text{amine})}{CH_3CH_2NH_2}$$

$$CH_3CH_2NH_2 + CH_3CH_2OH \xrightarrow[523K]{Al_2O_3} \underset{(2^\circ\text{amine})}{(CH_3CH_2)NH} + H_2O$$

$$(CH_3CH_2)_2NH + CH_3CH_2OH \xrightarrow[523\,K]{} \underset{3^\circ\text{amine}}{(CH_3CH_2)_3N} + H_2O$$

1.4 Physical properties of amines :

The properties of amines are as follows:

1. **Boiling Point :** Amines have higher boiling point due to the presence of H-bonds. But have lower boiling point than alcohols and carboxylic acids because $O-H$ bond present in alcohols and carboxylic acids are more polar than $N-H$ bonds in amines.

   Hydrocarbons $<$ Amines $<$ Alcohols $<$ Carboxylic Acids

2. **Solubility :** Lower amines are soluble in water due to hydrogen bonding with water molecules. Solubility decreases with increasing molecular mass due to the growing hydrophobic character of the alkyl group.

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1.5 Chemical properties of amines :

The Chemical properties of amines are as follow:

(i) **Reaction with water (basic nature) :** Due to the presence of lone pair on N-atom of the $-NH_2$ group, the aliphatic amines are basic in nature.

$$RNH_3 + H_2O \longrightarrow RNH_3^+ + OH^-$$

(a) Aliphatic amines are more basic than ammonia due to the presence of electron releasing alkyl group (+I effect).

(b) The secondary amines are the strongest bases among amines and basic strength varies as : 2°-amine$>1^\circ$-amine$>3^\circ$-amine due to the combined effect of inductive effect and solvation.

(c) Aniline is less basic than ethylamine due to the resonance in aniline in its benzene ring.

(d) Benzylamine is more basic than aniline because the lone pair or electrons on the N-atom in benzylamine is more readily available for protonation.

(ii) **Reaction with Acids With acids :** Amines being basic in nature react with acids to form salts. The amine donates its lone pair to the proton of the acid to form an alkylammonium salt.

$$CH_3NH_2 + HCl \longrightarrow \underset{\text{Methylammonium chloride}}{CH_3NH_2HCl}$$

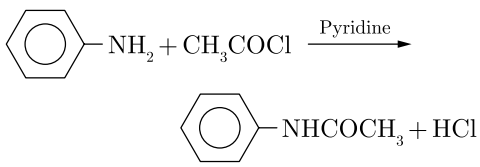
(iii) **Exhaustive alkylation :** When amines react with excess alkyl halide, all the hydrogen atoms on nitrogen are successively replaced by alkyl groups to form a quaternary ammonium salt. This reaction is called exhaustive alkylation or Hofmann's exhaustive methylation.

$$CH_3NH_2 \xrightarrow[-HCl]{+CH_3Cl} (CH_2)_2NH \xrightarrow[-HCl]{+CH_3Cl} (CH_3)_3N$$

$$+ CH_3Cl \, (CH_3)_4N^+Cl^-$$

(iv) **Acylation :** Primary and secondary amines react with acid chlorides or acid anhydrides in the presence of a base (pyridine) to form amides. This reaction is called acylation.

$$CH_3NH_2 + CH_3COCl \longrightarrow \underset{\text{N-Methylacetamide}}{CH_3NHCOCH_3} + HCl$$



Acetanilide

Tertiary amines do not respond because they lack replaceable hydrogen atom on nitrogen.

15. A student treated aniline with nitrous acid at low temperature and obtained benzene diazonium chloride. Which temperature is generally maintained during diazotisation?

ISC 2020

(a) 0–5°C
(b) 25–30°C
(c) 50–60°C
(d) Above 100°C

Ans : (a) 0–5°C

Diazotisation reactions are carried out at low temperature between 0–5°C because benzene diazonium salts are stable only under cold conditions. At higher temperatures diazonium salts decompose rapidly with evolution of nitrogen gas. Therefore careful temperature control is essential during preparation of diazonium compounds.

16. Which amine among the following possesses maximum basic strength in aqueous solution?

ISC 2017

(a) Ammonia
(b) Ethylamine
(c) Aniline
(d) Nitroaniline

Ans : (b) Ethylamine

Alkyl groups donate electron density towards nitrogen through positive inductive effect increasing availability of lone pair for protonation. Therefore ethylamine is more basic than ammonia. In aniline, resonance decreases availability of lone pair while nitro group in nitroaniline strongly withdraws electrons further reducing basic strength.

17. During exhaustive alkylation, trimethylamine reacts further with methyl iodide producing:

ISC 2011

(a) Primary amine
(b) Secondary amine
(c) Tertiary amine
(d) Quaternary ammonium salt

Ans : (d) Quaternary ammonium salt

In exhaustive alkylation, all hydrogen atoms attached to nitrogen are successively replaced by alkyl groups. Tertiary amines further react with alkyl halides producing quaternary ammonium salts containing four alkyl groups attached to positively charged nitrogen atom. The process is also called Hofmann exhaustive methylation.

18. A chemist compared the geometries of ammonia and amines. Which hybridisation is shown by nitrogen atom in amines?

ISC 2010

(a) sp
(b) sp^2
(c) sp^3
(d) dsp^2

Ans : (c) sp^3

In amines, nitrogen atom undergoes sp^3 hybridisation forming three sigma bonds and retaining one lone pair of electrons. Due to the presence of lone pair, the geometry becomes trigonal pyramidal rather than tetrahedral. Lone pair-bond pair repulsion decreases the bond angle below the ideal tetrahedral angle.

19. A student treated aniline with bromine water and observed formation of a white precipitate immediately. Which compound was formed during the reaction?

ISC 2011

(a) Bromobenzene
(b) p-Bromoaniline
(c) 2,4,6-Tribromoaniline
(d) m-Bromoaniline

Ans : (c) 2,4,6-Tribromoaniline

The amino group in aniline strongly activates the benzene ring through resonance effect increasing electron density particularly at ortho and para positions. Consequently bromination occurs rapidly even without catalyst producing white precipitate of 2,4,6-tribromoaniline. This reaction is commonly used as a qualitative test for aniline.

20. During diazotisation reaction, sodium nitrite and hydrochloric acid react together to generate which reagent in situ?

ISC Specimen 2024

(a) Nitric acid
(b) Nitrous acid
(c) Ammonia
(d) Hydroxylamine

Ans : (b) Nitrous acid

Sodium nitrite reacts with hydrochloric acid at low temperature producing nitrous acid in situ.

$NaNO_2 + HCl \rightarrow HNO_2 + NaCl$

Nitrous acid further reacts with primary aromatic amines forming diazonium salts. Since nitrous acid is unstable, it is always prepared freshly during the reaction.

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(ii) Isocyanides :

(a) From alkyl halides

$$RX + AgCN(alc.) \longrightarrow R{-}\overset{..}{N}{\equiv}C + AgX$$

(b) From primary amines (carbylamine reaction)

$$\underset{\text{Primary amine}}{R-NH_2} + CHCl_3 + 3KOH(alc.) \xrightarrow{\Delta}$$

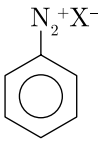
$$R-N\overset{..}{\equiv}C + 3KCl + 3H_2O$$
Alkyl isocyanide

3. DIAZONIUM SALTS

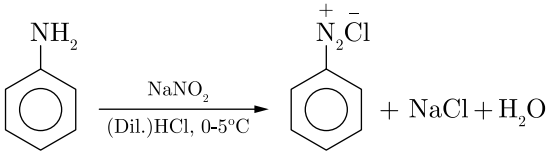
Dizonium salts have the general formula $RN_2^+X^-$, where X^- ion may be $Cl^-, Br^-, HSO_4^-, NO_3^-$ etc.

3.1 Structure of diazonium salts :

The diazonium slats have the general formula $ArN_2^+X^-$ and the group N_2^+ is called diazonium ion group.



3.2 Preparation of diazonium salts :



3.3 Physical properties of Diazonium Slats :

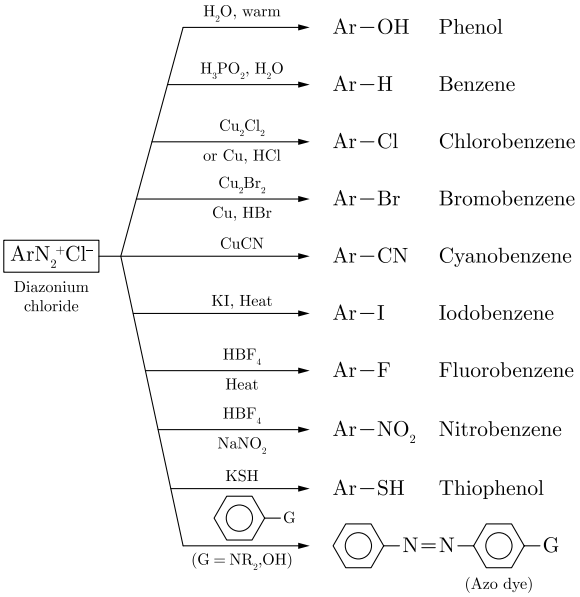
The physical properties of diazonium slats are as follows:

(i) They are readily soluble in water but less soluble in alcohol.

(ii) They are sued in solution state otherwise they explode in dry state.

3.4 Chemical Properties of Diazonium Salts :

The Chemical properties of diazonium salts are as follows:



OBJECTIVE QUESTIONS

1. On heating an aliphatic primary amine with chloroform and alc. potassium hydroxide, the organic compound formed is an

ISC 2020

(a) alkyl isocyanide (b) alkanol

(c) alkanal (d) alkyl cyanide

Ans : (a) alkyl isocyanide

$$RNH_2 + CHCl_3 + 3KOH(alc.) \xrightarrow{\Delta}$$

$$R-N\overset{..}{\equiv}C + 3KCl + H_2O$$
Alkyl isocyanide

2. Which of the following undergoes diazotisation?

(a) Aniline (b) Methylamine

(c) Ethylamine (d) All of these

ISC 2017

Ans : (a) Aniline

Diazotisation is the reaction of a primary aromatic amine with $NaNO_2$ and HCl at 0–5°C to form a stable diazonium salt.

$$\underset{\text{(aniline)}}{C_6H_5{-}NH_2} + NaNO_2 + HCl \rightarrow \underset{\text{(benzene diazonium chloride)}}{C_6H_5{-}N_2^+Cl^-} + NaCl + H_2O$$

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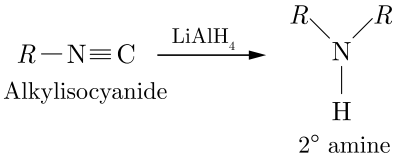
3. An alkyl isocyanide on complete reduction gives
ISC Specimen 2023

(a) primary amine (b) secondary amine
(c) tertiary amine (d) carboxylic acid

Ans : (b) secondary amine
Reduction of isocyanide gives secondary amine.
i.e.



4. Dehydration of an amide with phosphorus pentoxide yields
ISC 2006

(a) ammonia (b) alkyl cyanide
(c) alkyl isocyanide (d) alkyl amine

Ans : (b) alkyl cyanide
Dehydration of an amide with phosphorus pentaoxide yields alkyl cyanide.

5. The reaction of a primary amine with chloroform and ethanolic KOH is called
ISC 2023

(a) carbylamine reaction
(b) Kolbe's reaction
(c) Reimer-Tiemann reaction
(d) Wurtz-Fittig reaction

Ans : (a) carbylamine reaction
Carbylamine reaction Amine reacts with chloroform in the presence of base to give isocyanide which have foul smell. This reaction is only given by the primary amine.

$$R\text{NH}_2 + \text{CHCl}_3 + 3\text{KOH} \longrightarrow R\text{N} \equiv \text{C} + 3\text{KCl} + 3\text{H}_2\text{O}$$

6. Ethylamine ($C_2H_5NH_2$) reacts with nitrous acid (HNO_2) to form
ISC 2021-22 (Sem-II)

(a) methyl alcohol (b) ethyl alcohol
(c) ethane (d) ethyl nitrite

Ans : (b) ethyl alcohol

(b) $H_3C-CH_2-NH_2 \xrightarrow{NaNO_2 + HCl}$
Ethylamine

$$\left[H_3C-CH_2-\overset{\oplus}{N}\equiv N\right]\overset{\ominus}{Cl} \xrightarrow[-N_2\uparrow]{H_2O}$$
Ethyl diazonium salt

$$H_3C-CH_2-OH + HCl$$
Ethyl alcohol

Nitrous acid is used to distinguish between primary, secondary and tertiary amines with 1° amine, it liberates N_2 gas.
With 2° amine, it forms a yellow green oily layer.
With 3° amine, it forms water soluble salt.

7. The product formed when aniline is warmed with chloroform and caustic potash is
ISC 2010

(a) phenyl chloride
(b) methyl isocyanide
(c) phenyl isocyanide
(d) nitrophenol

Ans : (c) phenyl isocyanide
When a primary amine is warmed with chloroform ($CHCl_3$) and alcoholic KOH (caustic potash), it gives an isocyanide (carbylamine) with a foul smell.

$$\underset{\text{(aniline)}}{C_6H_5\text{-}NH_2} + CHCl_3 + 3KOH \rightarrow \underset{\text{(phenyl isocyanide)}}{C_6H_5\text{-}N\equiv C} + 3KCl + 3H_2O$$

8. Primary amine when warmed with chloroform and alc. KOH yields
ISC Specimen 2021-22 (Sem-II)

(a) cyanide
(b) isocyanide
(c) benzene diazonium chloride
(d) secondary amine

Ans : (b) isocyanide
Isocyanide is formed. It is the example of carbylamine reaction.

e.g. $\underset{\substack{\text{Ethylamine}\\(1^\circ\text{ amine})}}{CH_3CH_2NH_2} + CHCl_3 + 3KOH(\text{alc.}) \longrightarrow$

$$\underset{\text{Isocyanide}}{CH_3CH_2NC} + 3KCl + 3H_2\uparrow$$

NODIA

9. During qualitative analysis, a student treated an unknown organic compound with chloroform and alcoholic potassium hydroxide. A foul smelling compound was produced immediately. Which functional group is confirmed by this test?
ISC Specimen 2021

(a) Primary amine
(b) Secondary amine
(c) Tertiary amine
(d) Amide

Ans : (a) Primary amine

Primary amines react with chloroform and alcoholic potassium hydroxide producing foul smelling isocyanides or carbylamines. This reaction is called carbylamine reaction and is used as a confirmatory test for primary amines. Secondary and tertiary amines do not respond because they lack two hydrogen atoms attached to nitrogen.

10. A chemist compared the basic strengths of ethylamine and aniline. Ethylamine was found to be more basic. Which factor mainly explains this observation?
ISC Specimen 2019

(a) Resonance in aniline reduces availability of lone pair
(b) Ethylamine contains aromatic ring
(c) Aniline is non-polar
(d) Ethylamine lacks nitrogen atom

Ans : (a) Resonance in aniline reduces availability of lone pair

In aniline, the lone pair of electrons on nitrogen participates in resonance with the benzene ring and becomes partially delocalised. Consequently the lone pair becomes less available for protonation. In ethylamine, the lone pair remains localised and readily available, making ethylamine more basic than aniline.

11. Which named reaction converts amides into primary amines containing one carbon atom less?
ISC 2020

(a) Carbylamine reaction
(b) Hofmann degradation reaction
(c) Schotten-Baumann reaction
(d) Diazotisation reaction

Ans : (b) Hofmann degradation reaction

Hofmann degradation converts amides into primary amines using bromine and potassium hydroxide. During the reaction one carbon atom is lost in the form of carbon dioxide. Therefore the resulting amine contains one carbon atom less than the parent amide. The reaction is important for preparation of lower amines.

12. A student observed that methylamine is soluble in water whereas aniline is only sparingly soluble. Which factor mainly accounts for this difference?
ISC Specimen 2023

(a) Methylamine cannot form hydrogen bonds
(b) Aniline contains hydrophobic benzene ring
(c) Aniline is ionic in nature
(d) Methylamine lacks nitrogen atom

Ans : (b) Aniline contains hydrophobic benzene ring

Lower aliphatic amines dissolve readily in water because they form hydrogen bonds with water molecules. In aniline, the large hydrophobic benzene ring reduces overall polarity and decreases interaction with water molecules. Consequently aniline remains only sparingly soluble compared to methylamine.

13. During preparation of aniline from nitrobenzene, which process is generally employed?
ISC 2025

(a) Oxidation
(b) Reduction
(c) Nitration
(d) Sulphonation

Ans : (b) Reduction

Nitro compounds are commonly converted into amines through reduction reactions. Nitrobenzene undergoes reduction using reagents such as tin and hydrochloric acid, iron and hydrochloric acid or catalytic hydrogenation producing aniline. The nitro group is reduced stepwise into amino group without affecting the aromatic benzene ring.

14. A primary amine reacted with benzoyl chloride in presence of aqueous sodium hydroxide forming a benzamide derivative. Which named reaction is represented here?
ISC Specimen 2023

(a) Hofmann reaction
(b) Schotten-Baumann reaction
(c) Cannizzaro reaction
(d) Gattermann reaction

Ans : (b) Schotten-Baumann reaction

Schotten-Baumann reaction involves benzoylation of primary or secondary amines using benzoyl chloride in presence of aqueous sodium hydroxide. Benzamide derivatives formed are often crystalline solids and are useful for identification of amines.

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38. A chemist converted aniline into benzene diazonium chloride and further used it for preparation of chlorobenzene. Why are diazonium salts considered important intermediates in organic synthesis?

ISC Specimen 2018

(a) They are highly stable solids
(b) They easily undergo substitution reactions replacing diazonium group
(c) They are strong oxidising agents
(d) They do not react with nucleophiles

Ans : (b) They easily undergo substitution reactions replacing diazonium group

Diazonium salts readily undergo substitution reactions in which the diazonium group is replaced by various functional groups such as chlorine, bromine, hydroxyl and cyano groups. This versatility makes diazonium salts highly valuable intermediates for preparation of numerous aromatic compounds in organic synthesis.

39. **Assertion (A)** Nitration of chlorobenzene leads to the formation of *m*-nitrochlorobenzene.

Reason (R) Nitro ($—NO_2$) group is *m*-directing group.

ISC 2021-22 (Sem-II)

(a) Both (A) and (R) are correct and (R) is the correct explanation of (A).
(b) Both (A) and (R) are correct but (R) is not the correct explanation of (A).
(c) (A) is correct and (R) is incorrect.
(d) (A) is incorrect and (R) is correct.

Ans : (d) (A) is incorrect and (R) is correct.

(A) is incorrect but (R) is correct as the chlorination of nitrobenzene leads to the formation of *m*-nitrochlorobenzene because $-NO_2$ group deactivates the ring as it is *meta*-directing.

40. Assertion (A) : Benzylamine is more basic than aniline.
Reason (R) : In benzylamine, the lone pair on nitrogen is not involved in resonance with the benzene ring.

ISC Specimen 2007

(a) Both A and R are true and R is the correct explanation of A
(b) Both A and R are true but R is not the correct explanation of A
(c) A is true but R is false
(d) A is false but R is true

Ans : (a)

In benzylamine, the amino group is attached through a methylene group and therefore the lone pair remains available for protonation. In aniline, the lone pair participates in resonance with the benzene ring reducing its availability. Consequently benzylamine behaves as a stronger base than aniline.

41. Assertion (A) : Tertiary amines do not give carbylamine test.
Reason (R) : Tertiary amines lack hydrogen atoms attached to nitrogen atom.

ISC Specimen 2003

(a) Both A and R are true and R is the correct explanation of A
(b) Both A and R are true but R is not the correct explanation of A
(c) A is true but R is false
(d) A is false but R is true

Ans : (b)

Carbylamine reaction is shown only by primary amines because formation of isocyanides requires two hydrogen atoms attached to nitrogen. Tertiary amines completely lack hydrogen attached to nitrogen and therefore do not respond to this test. The absence of N-H bond prevents formation of the required intermediate.

42. Assertion (A) : Secondary amines are generally more basic than primary amines in aqueous solution.
Reason (R) : Secondary amines experience favourable inductive effect and effective solvation.

ISC 2008

(a) Both A and R are true and R is the correct explanation of A
(b) Both A and R are true but R is not the correct explanation of A
(c) A is false but R is true
(d) A is true but R is false

Ans : (d)

Secondary amines possess two electron donating alkyl groups which increase electron density on nitrogen through positive inductive effect. Their conjugate acids are also adequately solvated in water. These combined effects make secondary amines generally more basic than primary amines in aqueous medium.

43. Assertion (A) : Diazonium salts are generally used in solution state.
Reason (R) : Dry diazonium salts may decompose explosively.

ISC 2014

(a) Both A and R are false

NODIA

21. A primary aliphatic amine reacted with nitrous acid producing brisk effervescence due to liberation of nitrogen gas. Which product is generally formed simultaneously?

ISC Specimen 2009

(a) Alcohol
(b) Aldehyde
(c) Ketone
(d) Acid chloride

Ans : (a) Alcohol

Primary aliphatic amines react with nitrous acid forming unstable diazonium salts which immediately decompose liberating nitrogen gas. Water then replaces the diazonium group producing alcohols. The brisk evolution of nitrogen gas is characteristic of primary aliphatic amines and distinguishes them from secondary and tertiary amines.

22. A chemist observed that secondary amines are generally stronger bases than primary amines in aqueous solution. Which factor mainly contributes to this behaviour?

ISC 2006

(a) Resonance effect
(b) Combined inductive effect and solvation
(c) Presence of aromatic ring
(d) Absence of lone pair

Ans : (b) Combined inductive effect and solvation

Secondary amines possess two electron donating alkyl groups which increase electron density on nitrogen through positive inductive effect. At the same time, their conjugate acids remain sufficiently solvated in water. The combined influence of inductive effect and solvation makes secondary amines generally more basic than primary amines in aqueous solution.

23. A student prepared methyl cyanide from methyl bromide using alcoholic potassium cyanide. Which type of functional group is introduced during this conversion?

ISC 2002

(a) Amino group
(b) Carboxyl group
(c) Cyano group
(d) Nitro group

Ans : (c) Cyano group

Potassium cyanide reacts with alkyl halides through nucleophilic substitution introducing the cyano group ($-CN$). The carbon atom of cyanide ion attacks the alkyl halide producing nitriles or alkyl cyanides. This reaction is synthetically important because nitriles can further be converted into amines or carboxylic acids.

24. A laboratory assistant compared the boiling points of methylamine and methane. Methylamine exhibited much higher boiling point mainly because:

ISC Specimen 2021

(a) Methane contains stronger sigma bonds
(b) Methylamine forms intermolecular hydrogen bonding
(c) Methane is aromatic
(d) Methylamine contains ionic bonds

Ans : (b) Methylamine forms intermolecular hydrogen bonding

Amines contain nitrogen atoms with lone pair of electrons and hydrogen attached to nitrogen. Therefore molecules of primary and secondary amines can form intermolecular hydrogen bonds. Methane is non-polar and experiences only weak van der Waals forces. Consequently methylamine possesses much higher boiling point than methane.

25. A student treated ethylamine with acetyl chloride in presence of pyridine. Which product was formed during the reaction?

ISC 2010

(a) Ethanol
(b) Acetamide derivative
(c) Nitroethane
(d) Ethyl cyanide

Ans : (b) Acetamide derivative

Primary and secondary amines undergo acylation with acid chlorides in presence of bases such as pyridine forming substituted amides. Ethylamine reacts with acetyl chloride producing N-ethylacetamide. The reaction reduces the basic character of amines because the lone pair on nitrogen becomes delocalised in the amide group.

26. During reduction of nitriles using lithium aluminium hydride, which product is generally formed?

ISC 2005

(a) Alcohol
(b) Carboxylic acid
(c) Primary amine
(d) Ketone

Ans : (c) Primary amine

Nitriles undergo reduction with strong reducing agents such as lithium aluminium hydride producing primary amines. The cyano group is

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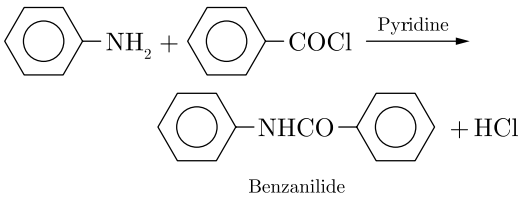
(v) **Benzoylation :** Amines react with benzoyl chloride (C_6H_5COCl) in the presence of aqueous NaOH to form benzamides. This is known as the Schotten–Baumann reaction.



Benzanilide

(vi) **With aldehydes :** Primary amines react with aldehydes to form Schiff's bases (aldimines) with the elimination of water.

$$RCHO + RNH_2 \longrightarrow \underset{\text{Schiff's base}}{R - CH = NR} + H_2O$$

(vii) **Oxidation :** Primary amines on oxidation with $KMnO_4$ or H_2O_2 give nitroso compounds, nitro compounds, or hydroxylamines depending on the conditions. Tertiary amines are oxidised by H_2O_2 to give amine oxides.

$$RCH_2NH_2 \xrightarrow[\text{Oxidation}]{KMnO_4/OH^-} RCH = NH$$

$$\xrightarrow[\text{Hydrolysis}]{H^+/H_2O} RCHO + NH_3$$

(viii) **Carbylamine reaction (Name Reaction) :**

$$CH_3CH_2NH_2 + CHCl_3 + 3KOH\,(alc.)$$

$$\xrightarrow{\Delta} \underset{\text{Ethyl isocyanide}}{CH_3CH_2NC} + 3KCl + 3H_2O$$

(ix) **Reaction with With nitrous acid :** Different classes of amines react differently with nitrous acid

$$RNH_2 + HNO_2 \longrightarrow \underset{\text{Alcohol}}{ROH} + N_2 + H_2O$$

$$R_2NH + HNO_2 \longrightarrow \underset{\text{Nitrosoamine}}{R_2N - N = O} + H_2O$$

(x) **Reaction with With Grignard reagent :**

$$RNH_2 + R'MgX \longrightarrow R'H + MgNHRX$$

$$R_2NH + R'MgX \longrightarrow R'H + MgNR_2X$$

(xi) **Hofmann mustard oil reaction (Name Reaction) :**

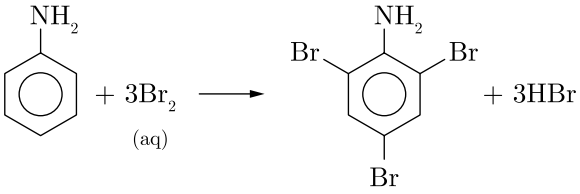
$$CH_3CH_2NH_2 + CS_2 \xrightarrow{\Delta} CH_3CH_2NH-\overset{S}{\overset{\|}{C}}-SH$$

$$\xrightarrow[HgCl_2]{\Delta} \underset{\text{Ethyl isothiocyanate}}{CH_3CH_2-N=C=S} + HgS + 2HCl$$

(xii) **With phosgene :**

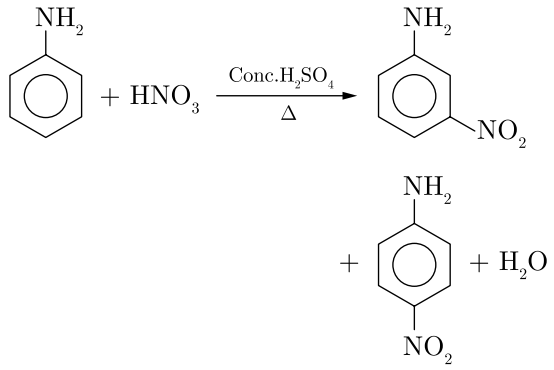
$$2RNH_2 + COCl_2 \longrightarrow RNH - \overset{S}{\overset{\|}{C}} - NH - R + 2HCl$$

(xiii) **Bromination :**



2,4,6 - tribromoaniline

(xiv) **Nitration :**



2. CYANIDES AND ISOCYANIDES

The cyanide group is an ambident group and can attach itself to H through both C as well as N-atom.

HCN exists in the following two tautomeric forms

$$\underset{\text{Hydrogen cyanide}}{H - C \equiv N} \rightleftharpoons \underset{\text{Hydrogen isocyanide}}{H - N \overset{+}{=} C}$$

The functional group in cyanides in $-C \equiv N$ and is called cyano or nitrile group, while that in isocyanides is $-N \overset{+}{=} C$ and is called isocyano or isonitrile or carbylamine group.

2.1 General Methods for the Preparation of Cyanides and Isocyanides

(i) Cyanides

(a) From alkyl halides

$$RX + K^+CN^-(alc.) \xrightarrow{\Delta} R - C \equiv N + K^+X^-$$

(b) From acid amides

$$R - \overset{O}{\overset{\|}{C}} - NH_2 \xrightarrow[\Delta]{P_2O_5 \text{ or } SOCl_2} R - C \equiv N + H_2O$$

Ans : (c) Phenol

Benzene diazonium chloride undergoes hydrolysis on warming with water producing phenol with liberation of nitrogen gas.

$C_6H_5N_2Cl + H_2O \rightarrow C_6H_5OH + N_2 + HCl$

This reaction is synthetically important because diazonium salts serve as useful intermediates for preparation of aromatic compounds.

33. During comparison of boiling points, dimethylamine was found to have lower boiling point than ethanol. Which factor mainly explains this observation?

ISC Specimen 2023

(a) Amines are ionic compounds
(b) Hydrogen bonding in alcohols is stronger than in amines
(c) Ethanol is non-polar
(d) Amines lack lone pair electrons

Ans : (b) Hydrogen bonding in alcohols is stronger than in amines

Both alcohols and amines form intermolecular hydrogen bonds, but oxygen is more electronegative than nitrogen. Consequently hydrogen bonding in alcohols is stronger than in amines. Stronger intermolecular attraction in ethanol requires greater energy to separate molecules during boiling, resulting in higher boiling point.

34. A student observed that tertiary amines do not undergo acylation reactions. What is the main reason for this behaviour?

ISC 2004

(a) Tertiary amines are acidic
(b) They lack lone pair electrons
(c) They do not possess replaceable hydrogen atom attached to nitrogen
(d) They are insoluble in organic solvents

Ans : (c) They do not possess replaceable hydrogen atom attached to nitrogen

Acylation reactions involve replacement of hydrogen atom attached to nitrogen by acyl group. Tertiary amines contain three alkyl groups attached to nitrogen and therefore lack replaceable hydrogen atom. Consequently they do not undergo acylation unlike primary and secondary amines which possess hydrogen attached to nitrogen.

35. A chemist reduced an alkyl cyanide using lithium aluminium hydride and obtained propylamine. Which nitrile was most likely used as the starting compound?

ISC 2009

(a) Ethyl cyanide
(b) Methyl cyanide
(c) Propyl cyanide
(d) Benzyl cyanide

Ans : (a) Ethyl cyanide

Reduction of nitriles converts the cyano group into amino group without changing the number of carbon atoms.

$C_2H_5CN \xrightarrow{LiAlH_4} C_3H_7NH_2$

Therefore ethyl cyanide or propionitrile produces propylamine after reduction. This method is widely used for synthesis of higher primary amines.

36. During bromination of aniline, why does substitution occur readily at ortho and para positions without catalyst?

ISC Specimen 2021

(a) Amino group withdraws electrons strongly
(b) Amino group activates benzene ring through resonance
(c) Bromine behaves as reducing agent
(d) Aniline lacks aromatic character

Ans : (b) Amino group activates benzene ring through resonance

The amino group donates electron density into the benzene ring through resonance increasing electron density particularly at ortho and para positions. As a result electrophilic substitution reactions occur rapidly even without catalyst. Therefore aniline undergoes bromination readily producing 2,4,6-tribromoaniline as the major product.

37. A primary aromatic amine was treated with nitrous acid at low temperature forming a stable diazonium salt. Which amine shows this behaviour?

ISC 2025

(a) Methylamine
(b) Ethylamine
(c) Aniline
(d) Trimethylamine

Ans : (c) Aniline

Primary aromatic amines such as aniline react with nitrous acid at 0–5°C producing relatively stable diazonium salts. Aromatic diazonium salts are stabilised by resonance with the benzene ring. Primary aliphatic diazonium salts are unstable and immediately decompose liberating nitrogen gas.

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converted into amino group without changing the carbon chain length. This method is important in synthetic organic chemistry because it provides convenient preparation of higher primary amines.

27. A chemist compared aniline and benzylamine for their basic strengths. Benzylamine was found to be more basic because:

ISC 2002

(a) Benzylamine lacks nitrogen atom
(b) Lone pair in benzylamine is more available for protonation
(c) Aniline contains hydrogen bonding
(d) Benzylamine is non-polar

Ans : (b) Lone pair in benzylamine is more available for protonation

In aniline, the lone pair on nitrogen participates in resonance with the benzene ring and becomes less available for protonation. In benzylamine, the amino group is attached through a methylene group and therefore resonance does not occur. Consequently the lone pair remains more available making benzylamine more basic.

28. During preparation of diazonium salts, why are dry diazonium salts generally not isolated?

ISC Specimen 2022

(a) They are highly acidic
(b) They are insoluble in water
(c) They may explode in dry state
(d) They readily form alcohols

Ans : (c) They may explode in dry state

Diazonium salts are generally stable only in cold aqueous solution. In dry state many diazonium salts become highly unstable and may decompose explosively with liberation of nitrogen gas. Therefore diazonium salts are usually prepared and used immediately in solution form under carefully controlled low temperature conditions.

29. A student reacted ethylamine with chloroform and alcoholic potassium hydroxide during a laboratory test. A highly unpleasant smelling compound was produced. Which compound was formed?

ISC 2011

(a) Ethyl cyanide
(b) Ethyl alcohol
(c) Ethyl isocyanide
(d) Ethyl nitrite

Ans : (c) Ethyl isocyanide

Primary amines react with chloroform and alcoholic potassium hydroxide producing isocyanides or carbylamines having extremely unpleasant smell.

$$C_2H_5NH_2 + CHCl_3 + 3KOH \rightarrow C_2H_5NC + 3KCl + 3H_2O$$

This reaction is called carbylamine reaction and serves as a confirmatory test for primary amines.

30. During preparation of primary amines from alkyl halides using excess ammonia, multiple products are often formed. Which reaction explains this process?

ISC 2019

(a) Diazotisation
(b) Hofmann ammonolysis
(c) Gattermann reaction
(d) Sandmeyer reaction

Ans : (b) Hofmann ammonolysis

Hofmann ammonolysis involves reaction of alkyl halides with alcoholic ammonia producing primary amines. However, the primary amines formed are more nucleophilic than ammonia and may react further with alkyl halides producing secondary, tertiary amines and quaternary ammonium salts. Excess ammonia is used to favour formation of primary amines.

31. A chemist converted ethanamide into methylamine using bromine and potassium hydroxide. Which important feature distinguishes this reaction?

ISC 2008

(a) Increase in carbon chain length
(b) Retention of carbon atoms
(c) Decrease in carbon chain length by one carbon atom
(d) Formation of alcohols only

Ans : (c) Decrease in carbon chain length by one carbon atom

In Hofmann degradation reaction, amides react with bromine and potassium hydroxide producing primary amines containing one carbon atom less than the parent amide. Carbonyl carbon is removed during the reaction. Thus ethanamide forms methylamine, making this reaction important for preparation of lower amines.

32. A student treated benzene diazonium chloride with warm water and obtained a phenolic compound. Identify the product formed.

ISC 2001

(a) Benzene
(b) Aniline
(c) Phenol
(d) Nitrobenzene

NODIA

(b) A is false but R is true
(c) Both A and R are true and R is the correct explanation of A
(d) A is true but R is false

Ans : (c) Both A and R are true and R is the correct explanation of A

Diazonium salts are unstable compounds and many of them decompose violently in dry state with liberation of nitrogen gas. Therefore they are generally prepared and used immediately in cold aqueous solution. Their instability makes careful handling essential during organic synthesis involving diazonium intermediates.

44. Assertion (A) : Aniline undergoes bromination readily without catalyst.
Reason (R) : Amino group activates the benzene ring through resonance effect.
ISC 2018

(a) A is true but R is false
(b) Both A and R are true and R is the correct explanation of A
(c) Both A and R are false
(d) A is false but R is true

Ans : (b) Both A and R are true and R is the correct explanation of A

The amino group donates electron density into the benzene ring through resonance effect increasing electron density particularly at ortho and para positions. Consequently electrophilic substitution reactions such as bromination occur rapidly even without catalyst producing 2,4,6-tribromoaniline as the major product.

FILL IN THE BLANK

45. Basicity of aniline is _____ than that of ammonia because of _____
ISC 2000

Ans :

Basicity of aniline is less than that of ammonia because of inductive $(-I)$ effect.

46. Methylamine is more _____ than ammonia because of _____ effect.
ISC 2002

Ans :

Methylamine is more basic than NH_3 (ammonia) because of inductive $(+I)$ effect.

47. When acetamide is treated with bromine and caustic soda, it gives _____ as the main product and the reaction is called _____
ISC 2011

Ans :

When acetamide is treated with bromine and caustic soda, it gives methylamine as the main product and the reaction is called Hofmann's degradation.

ONE MARK QUESTIONS

48. Give a chemical test to distinguish between ethylamine and diethylamine.
ISC 2014

Ans :

Hinsberg's test can distinguish between (1°) ethylamine and (2°) diethylamine.

49. Explain the following with at least one example:
Carbylamine reaction
ISC 2007

Ans :

Carbylamine reaction

$$R\text{NH}_2 + \text{CHCl}_3 + 3\text{KOH} \longrightarrow R\text{NC} + 3\text{KCl} + 3\text{H}_2\text{O}$$

50. Give reason.
Direct nitration of aniline is not possible.
ISC 2007

Ans :

Direct nitration of aniline gives oxidation products alongwith some nitro derivatives therefore direct nitration is not possible.

51. Give the balanced equation for carbylamine reaction.
ISC 2016

Ans :

Carbylamine reaction

$$R\text{NH}_2 + \text{CHCl}_3 + 3\text{KOH} \longrightarrow R\text{NC} + 3\text{KCl} + 3\text{H}_2\text{O}$$

52. Give balanced equation when ethylamine is heated with chloroform and alcoholic solution of potassium hydroxide.
ISC 2019

Ans :

$$\underset{\text{Ethylamine}}{\text{CH}_3\text{CH}_2\text{NH}_2} + \underset{\text{Chloroform}}{\text{CHCl}_3} + 3\text{KOH(alc.)} \xrightarrow{\Delta}$$

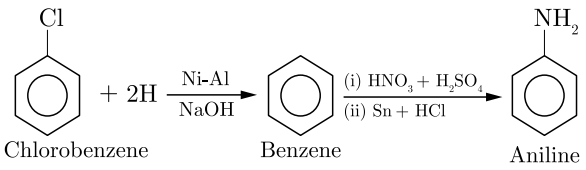
$$\underset{\text{Ethyl isocyanide}}{\text{CH}_3\text{CH}_2\text{—N}\rightleftharpoons\text{C}} + 3\text{KCl} + 3\text{H}_2\text{O}$$

NODIA

53. Convert chlorobenzene to aniline.

ISC 2020

Ans :

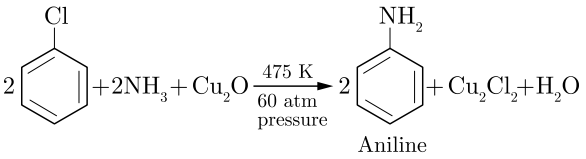


54. Write a chemical equation of chlorobenezene treated with ammonia in the presence of Cu_2O at 475 K and 60 atm.

ISC 2019

Ans :

Chlorobenzene when treated with ammonia in the presence of Cu_2O at 475 K and 60 atm pressure form aniline.

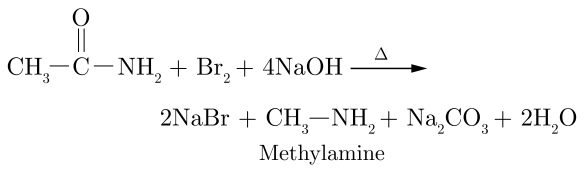


55. Give the balanced equation for Hofmann's degradation reaction.

ISC 2015

Ans :

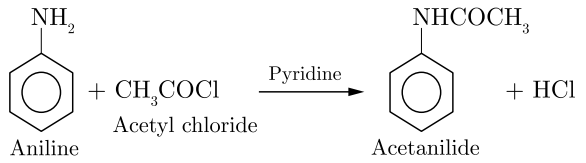
Hofmann's degradation reaction



56. Write the equation for the preparation of acetanilide from aniline.

ISC 2014

Ans :



This reaction is known as acetylation.

57. Write the balanced chemical equation for the following reaction and name the reaction. Acetamide is heated with bromine and sodium hydroxide solution.

ISC 2013

Ans :

$$\underset{\text{Acetamide}}{CH_3CONH_2} + Br_2 + 4NaOH \longrightarrow \underset{\text{Methylamine}}{CH_3NH_2} + 2NaBr + Na_2CO_3 + 2H_2O$$

This reaction is known as Hofmann- bromamide reaction.

58. Complete the following reaction and name the reaction.

ISC 2012

$$C_3H_7NH_2 + CHCl_3 + 3KOH(alc.) \xrightarrow{\Delta} ..... + 3KCl + 3H_2O$$

Ans :

$$C_3H_7NH_2 + CHCl_3 + 3KOH(alc.) \xrightarrow{\Delta} C_3H_7NC + 3KCl + 3H_2O$$

This reaction is called carbylamine reaction.

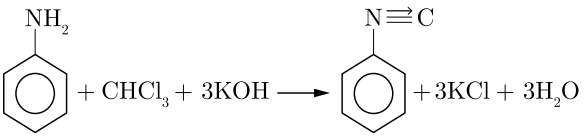
59. Give the balanced equation for the following. Acetamide is heated with sodium hydroxide.

ISC 2011

Ans :

$$\underset{\text{Acetamide}}{CH_3CONH_2} + NaOH \xrightarrow{\text{Boil}} \underset{\text{Sodium acetate}}{CH_3COO^-Na^+} + NH_3$$

This reaction is called hydrolysis of amide in alkaline conditions.

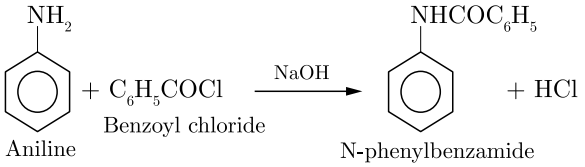


60. Give the balanced equation for the following reaction.

Aniline is treated with benzoyl chloride.

ISC 2009

Ans :



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61. How can the following conversion be brought about?

Acetic acid to methyl cyanide

ISC 2014

Ans :

$$CH_3COOH \xrightarrow[\text{(ii) Heat}]{\text{(i) } NH_3} CH_3CONH_2 \xrightarrow{P_2O_3,\Delta} CH_3CN$$

Acetic acid — Methyl cyanide

62. Give one example of the following name reaction.

Hofmann's degradation

ISC 2008

Ans :

Hofmann's degradation reaction

$$CH_3-\overset{\overset{O}{\|}}{C}-NH_2 + Br_2 + 4NaOH \xrightarrow{\Delta}$$

$$2NaBr + \underset{\text{Methylamine}}{CH_3-NH_2} + Na_2CO_3 + 2H_2O$$

63. How would you convert the following?

Methylamine to ethylamine

ISC 2007

Ans :

Methylamine to ethylamine

$$\underset{\text{Methylamine}}{CH_3NH_2} \xrightarrow{HNO_2} CH_3OH \xrightarrow{PCl_5} CH_3Cl \xrightarrow{NaCN}$$

$$CH_3CN \xrightarrow{LiAlH_4} \underset{\text{Ethylamine}}{CH_3CH_2NH_2}$$

64. Write the balanced chemical equation for the following and name the reaction.

Aniline is warmed with chloroform and alcoholic potassium hydroxide.

ISC 2006, 2002

Ans :

$$\underset{\text{Aniline}}{C_6H_5NH_2} + CHCl_3 + \underset{\text{(Alc.)}}{3KOH} \longrightarrow$$

$$\underset{\text{Phenyl isocyanide}}{C_6H_5NC} + 3KCl + 3H_2O$$

The reaction is carbylamine reaction.

65. Name the following reaction and write balanced equation. Acetamide with bromine in the presence of potassium hydroxide.

ISC 2002

Ans :

This reaction is Hofmann's degradation.

$$\underset{\text{Acetamide}}{CH_3CONH_2} + Br_2 + 4KOH \longrightarrow$$

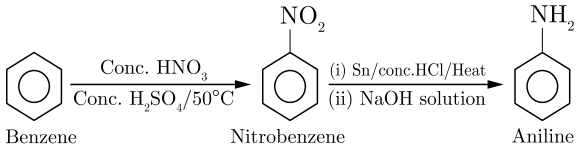
$$\underset{1^\circ \text{ amine}}{CH_3NH_2} + 2KBr + K_2CO_3 + 2H_2O$$

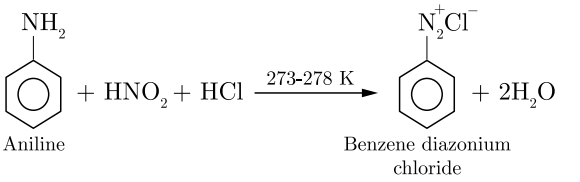
NODIA

66. Convert benzene to benzene diazonium chloride.

ISC 2016

Ans :



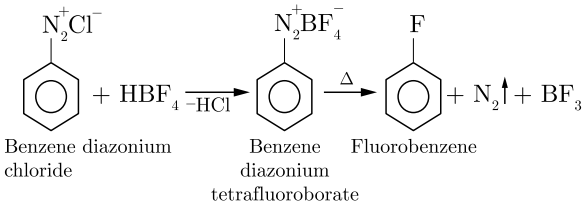


67. Give balanced equation for the following name reaction: Balz-Schiemann's reaction

ISC 2014

Ans :

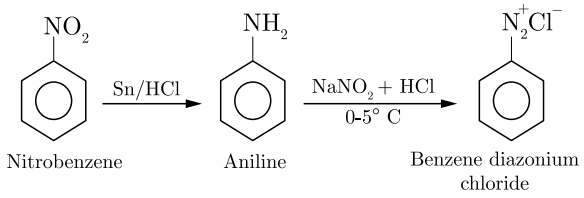
Balz-Schiemann's reaction



68. How can the following conversion be brought about? Nitrobenzene to benzene diazonium chloride

ISC 2013

Ans :



69. Give balanced equation for the following reaction given below.

Aniline is treated with a mixture of $NaNO_2$ and excess of HCl at low temperature.

ISC 2007

Ans :

$$C_6H_5NH_2 + HNO_2 + HCl \xrightarrow[\text{HCl at low temperature}]{NaNO_2}$$

$$C_6H_5\overset{+}{N} \equiv N\bar{Cl} + 2H_2O$$

95. How will you distinguish between primary, secondary and tertiary amines by Hinsberg test?

ISC 2012

Ans :

The mixture of amines is treated with benzene sulphonyl chloride (Hinsberg's reagent) and shaken with alkali solution.

1. Primary amine forms alkyl benzenesulphonamide which dissolves in alkali to form sodium or potassium salt of monoalkylbenzenesulphonamide.
$$PhSO_2Cl + HNHR \rightarrow PhSO_2NHR \xrightarrow{KOH}$$
$$PhSO_2NKR \text{ (water soluble)}$$
2. Secondary amine forms alkyl sulphonamide which does not form salt with alkali and hence remains insoluble (solid) in alkali solution.
$$PhSO_2Cl + HNR_2 \rightarrow PhSO_2 \text{(water insoluble)}$$
$$\rightarrow \text{no action}$$
3. Tertiary amines does not react with Hinsberg's reagent.
$$PhSO_2Cl + NR_3 \rightarrow \text{no reaction}$$

96. State reasons for the following.

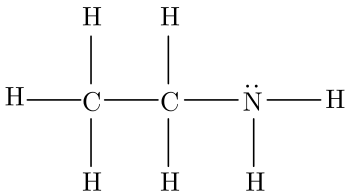
(i) Ethylamine is soluble in water, whereas aniline is insoluble in water.

(ii) Aliphatic amines are stronger bases than aromatic amines.

ISC Specimen 2023, 2020

Ans :

(i) Ethylamine is soluble in water, whereas aniline is insoluble. This is because:
Ethylamine is capable of forming hydrogen bonds with water as it is soluble but aniline the bulk carbon prevents the formation of effective hydrogen bonding and is not soluble. Ethylamine ($C_2H_5NH_2$) in addition to water forms intermolecular H-bonds with water. It is soluble in the water.



(ii) In aliphatic amines, the $-NH_2$ group is attached to an alkyl group which is an electron donating group i.e, they have + I effect. So, the lone pair of electrons on nitrogen are readily available.

In aromatic amines, the $-NH_2$ group is attached to a $-C_6H_5$ group, which is an electron withdrawing group. So, the availability of a lone pair of electrons on is decreased. Therefore aliphatic amines are more basic than aromatic amines.

97. Write balanced chemical equations for carbylamine reaction and diazotisation reaction.

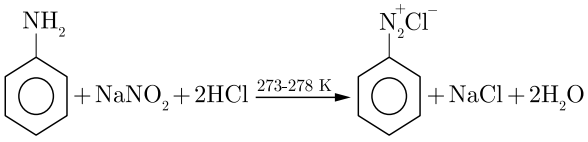
ISC 2018

Ans :

Carbylamine reaction Aliphatic or aromatic amines on heating with chloroform and alcoholic KOH forms isocyanides or carbylamines which are foul smelling substances.

$$\underset{\text{Amine}}{R-NH_2} + \underset{\text{Chloroform}}{CHCl_3} + 3KOH \xrightarrow{\Delta}$$
$$\underset{\text{Alkyl or aryl isocyanide}}{R-NC} + 3KCl + 3H_2O$$

Diazotisation reaction Diazonium salts can be prepared by diazotisation. In this reaction, ice-cold solution of $HNO_3(NaNO_2 + HCl + NaNO_2 + H_2SO_4)$ is added to ice-cold solution of primary aromatic amine dissolved in acid to form diazonium salt.



98. Give the balanced equations for following reactions.

(i) How will you convert ethylamine to methylamine?

(ii) Aniline is treated with nitrous acid and HCl at low temperature.

ISC 2016

Ans :

(i) $\underset{\text{Ethylamine}}{CH_3-CH_2-NH_2} + HNO_2 \xrightarrow{\text{Cold}}$
$$CH_3-CH_2-OH + N_2\uparrow + H_2O$$
$$CH_3-CH_2-OH + [O] \xrightarrow[\text{Dil. } H_2SO_4, \Delta]{K_2Cr_2O_7}$$
$$CH_3COOH + H_2O$$
$$CH_3COOH \xrightarrow{SOCl_2} CH_3COCl \xrightarrow{NH_3}$$
$$CH_3CONH_2 \xrightarrow{Br_2+NaOH} \underset{\text{Methylamine}}{CH_3NH_2}$$

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76. Arrange the following in the increasing order of their basic strength; $C_2H_5NH_2$, $C_6H_5NH_2$, $(C_2H_5)_2NH$.

Ans : ISC Specimen 2021-22 (Sem-II)

Due to $-I$-effect to C_6H_5 group, the electron density of N-atom in $C_6H_5NH_2$ is lower than that of $C_2H_5NH_2$. So, $C_6H_5NH_2$ is least basic while in case of $C_2H_5NH_2$ and $(C_2H_5)_2NH$, considering the inductive effect and steric hindrance of alkyl group.

The increasing order of basic strength is

$$C_6H_5CH_2 < C_2H_5NH_2 < (C_2H_5)_2NH$$

77. $CH_3NH_2 + CHCl_3 + 3KOH(alc.) \xrightarrow{Heat}$

$$.....3KCl + 3H_2O$$

(a) Complete the reaction given above.

(b) Name the reaction given above.

ISC 2022 (Sem-II)

Ans :

(a) $CH_3NH_2 + CHCl_3 + 3KOH(alc.) \xrightarrow{\Delta}$

$CH_3{-}N{\equiv}C + 3KCl + 3H_2O$

(b) This reaction is called as carbylamine reaction.

78. State the reagents for the following conversion.

Benzene $\xrightarrow{[A]}$ Nitrobenzene $\xrightarrow{[B]}$ Aniline $\xrightarrow{[C]}$ Aniline hydrochloride $\xrightarrow{[D]}$ Benezene diazonium chloride

ISC 2008

Ans :

Benzene $\xrightarrow[\text{Conc. } H_2SO_4]{\text{Conc. } HNO_3 \text{ and}}$ Nitrobenzene $\xrightarrow[[B]]{Sn/HCl}$

Aniline $\xrightarrow[[C]]{HCl}$ Aniline hydrochloride $\xrightarrow[[D]5^\circ C]{NaNO_2+HCl}$

Benzene diazonium chloride

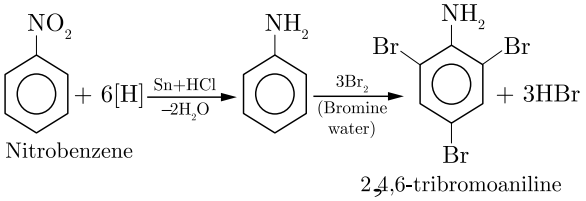
79. How can the following conversion be brought about?

Nitrobenzene to 2, 4, 6-kibromoaniline

ISC 2014

Ans :

Nitrobenzene to 2, 4, 6-tribromoaniline



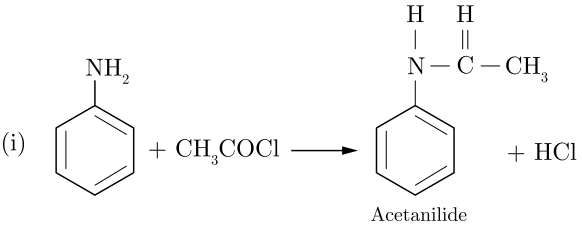
80. Complete and balance the following equations.

(i) $C_6H_5NH_2 + CH_3COCl \longrightarrow ... + ...$

(ii) $C_2H_5NH_2 + HNO_2 \longrightarrow ... + ... + ...$

ISC 2020

Ans :

(i) 

(ii) $C_2H_5NH_2 + HNO_2 \longrightarrow C_2H_5OH + N_2\uparrow + HCl$

81. Acetamide is amphoteric in nature. Give two equations to support this statement.

ISC 2013

Ans :

Acetamide is formed from weak acid (CH_3COOH) and a weak base (NH_3).

Basic nature

$$CH_3CONH_2 + HCl \longrightarrow CH_3C\overset{+}{O}NH_3Cl^-$$

Acidic nature

$$2CH_3CONH_2 + HgO \longrightarrow (CH_3CONH)_2Hg + H_2O$$

82. How will you distinguish between the following pair of compounds? Give one chemical test.

Ethylamine and acetamide

ISC 2009

Ans :

Ethylamine (1° amine) when heated with chloroform and alcoholic KOH it forms ethyl carbylamine which has peculiar offensive smell.

Acetamide (acid amide) does not give this test.

$$CH_3CH_2NH_2 + CHCl_3 + KOH(alc.) \xrightarrow{\Delta}$$

$$\underset{\text{(Four smell)}}{CH_3CH_2NC} + 3KCl + 3H_2O$$

83. How will you carry out the following conversion?

Write the balanced equation and name the reaction.

Acetamide to methylamine

ISC 2001, 2000

Ans :

Acetamide can be converted to methylamine by the reaction of acetamide with bromine in the presence of alkali solution.

NODIA

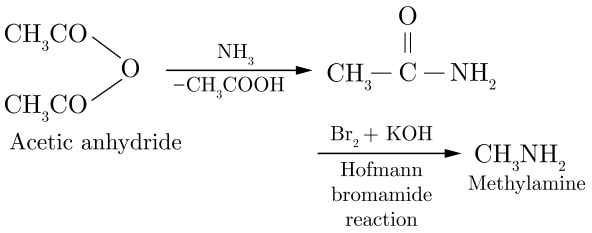
70. How will you convert the acetic anhydride to methylamine?

ISC 2004

Ans :

Ans :

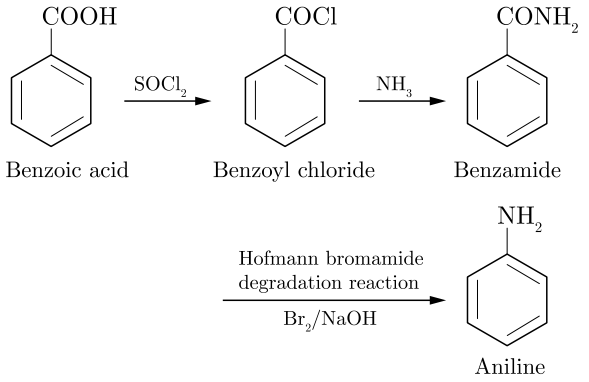
Acetic anhydride to methylamine



71. Convert benzoic acid to aniline.

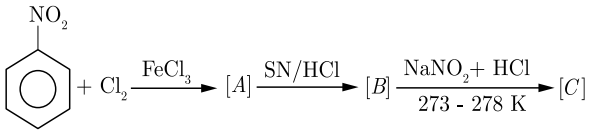
ISC 2016

Ans :

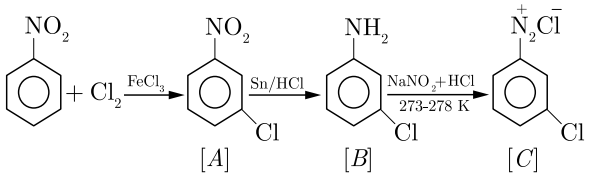


72. Complete the following reaction and name the intermediate products A, B and C.

ISC 2006



Ans :



A is m-chloronitrobenzene

B is m-chloroaniline

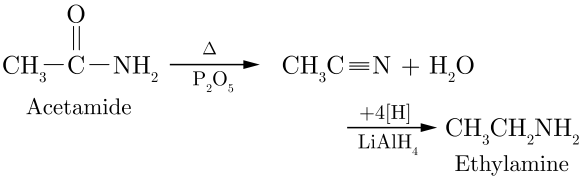
C is m-chlorobenzene diazonium chloride

73. How will you carry out the following conversion?
Acetamide to ethylamine

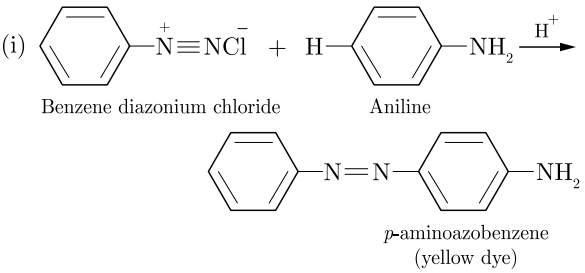
ISC 2003

Ans :

Acetamide to ethylamine



Ans :

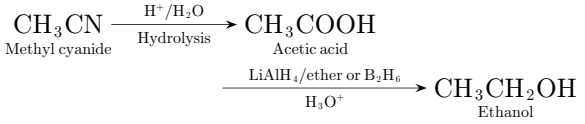


TWO MARKS QUESTIONS

74. Give a balanced chemical equation to convert methyl cyanide to ethyl alcohol.

ISC 2018

Ans :



75. Identify the reagents, X, Y and Z.

$$C_2H_5Cl \xrightarrow{[X]} C_2H_5CN \xrightarrow{[Y]} C_2H_5CH_2NH_2 \xrightarrow{Z} C_2H_5CH_2NHCOCH_3$$

ISC 2012

Ans :

$$C_2H_5Cl \xrightarrow[[X]]{KCN} C_2H_5CN \xrightarrow[[Y]]{Na/C_2H_5OH}$$

$$C_2H_5CH_2NH_2 \xrightarrow[[Z]]{(CH_3CO)_2O} C_2H_5CH_2NHCOCH_3$$

$X = KCN$, $Y = Na/C_2H_5OH$, $Z = (CH_3CO)_2O$

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In aniline, the lone pair of nitrogen is in conjugation with benzene and less available for protonation hence, aniline is less basic than aliphatic amine and ethers are inert in nature due to stable C – O – C bond.

90. Give one good chemical test to distinguish between the following pair of organic compounds.
Methylamine and dimethylamine

ISC 2011

Ans :

Methylamine (1°) and dimethyl amine (2°) can be distinguished by carbylamine test.

Methylamine when heated with chloroform and alcoholic potassium hydroxide, it forms methyl isocyanide commonly known as carbylamine which can be recognised once by its offensive odour but this test is not responded by dimenthylamine because it is secondary amine.

$$\underset{\text{Methylamine}}{CH_3NH_2} + CHCl_3 + 3KOH(alc.) \xrightarrow{\Delta} CH_3NC + 3KCl + 3H_2O$$

91. Give balanced equation for each of the following.

(i) Ethylamine and nitrous acid

(ii) Aniline and acetyl chloride

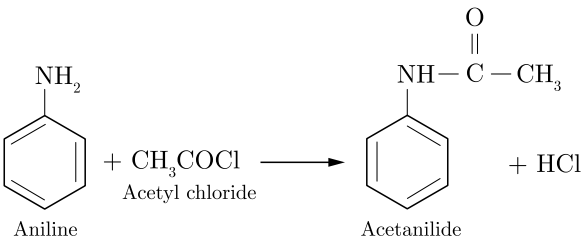
ISC Specimen 2021-22 (Sem-II), 2016

Ans :

(i) Reaction between ethylamine and nitrous acid

$$\underset{\text{Ethylamine}}{CH_3CH_2NH_2} + \underset{\text{Nitrous acid}}{HNO_2} \longrightarrow \underset{\text{Ethanol}}{CH_3CH_2OH} + H_2O + N_2\uparrow$$

(ii) Reaction between aniline and acetyl chloride



92. State one reason for each of the following.

ISC 2023

(i) Alkylamine is soluble in water, whereas arylamine is insoluble in water.

(ii) Methylamine is a stronger base than methyl alcohol.

Ans :

(i) Alkylamine forms intermolecular hydrogen bonding with water molecules when mixed with water. Hence, it is soluble in water.

On the other hand, arylamine has large hydrophobic C_6H_5 group which do not allow to form H-bonds to greater extent.
Therefore, it is insoluble in water.

(ii) In methylamine $(MeNH_2)$, nitrogen is less electronegative than oxygen in methyl alcohol. So, methylamines can easily donate a lone pair of electrons to a proton of an acid and hence are stronger base than methyl alcohol.

93. Give two tests to distinguish between aniline and dimethyl aniline.

ISC 2008, 2000

Ans :

(i) Carbylamine reaction

Aniline [1° **amine**]	**Dimethyl aniline** [2° amine]
Aniline gives four smell of phenyl isocyanide, when heated with chloroform and KOH. $C_6H_5NH_2 + CHCl_3 + 3KOH \longrightarrow C_6H_5NC + 3KCl + 3H_2O$	No characteristic observation.

(ii) Dye test

On diazotisation and coupling with alkaline β-naphthol, aniline forms an orange red dye.	No characteristic observation.

94. Arrange the following in the increasing order of their basic strength.

$$C_2H_5NH_2,\ C_6H_5NH_2,\ (C_2H_5)_2NH$$

ISC 2018

Ans :

Basic character of amines depends upon the availability of lone pair of electrons on nitrogen for donation.

Presence of electron releasing group increases the electron density over nitrogen, thus lone pair of nitrogen are available for donation. Hence, basic character increases. Due to resonance in aniline, lone pair of electron gets delocalised inside the benzene ring, thus it is less available for protonation.

Thus, the correct increasing order of basic strength is

$$C_6H_5NH_2 < C_2H_5NH_2 < (C_2H_5)_2NH$$

NODIA

103. Identify A, B and C.

$$CH_3CONH_2 \xrightarrow[\Delta]{P_2O_5} [A] \xrightarrow{H_2/Pt} [B] \xrightarrow[HCl]{NaNO_2} [C]$$

ISC 2002

Ans :

$$CH_3CONH_2 \xrightarrow[\Delta]{P_2O_5} \underset{[A]}{CH_3CN} + H_2O$$

$$\underset{[A]}{CH_3CN} \xrightarrow[\Delta]{H_2/pt} \underset{[B]}{CH_3CH_2NH_2}$$

$$CH_3CH_2NH_2 \xrightarrow[HCl]{NaNO_2} \underset{[C]}{CH_3CH_2OH} + N_2\uparrow + H_2O$$

$A \rightarrow$ methyl cyanide,

$B \rightarrow$ Ethylamine,

$C \rightarrow$ Ethyl alcohol.

104. How can the following conversion be brought about?

Ethylamine to methylamine

ISC 2010, 2000

Ans :

Ethylamine to methylamine

$$\underset{\text{Ethylamine}}{CH_3CH_2 \cdot NH_2} \xrightarrow[-NH_2, -H_2O]{+HNO_2} \underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[\Delta]{Cu/573\,K}$$

$$\underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow[KMnO_4]{\text{Alkaline}} \underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{SOCl_2}$$

$$\underset{\text{Acetyl chloride}}{CH_3COCl} \xrightarrow[-H_2O]{NH_3/\Delta} \underset{\text{Acetamide}}{CH_3CONH_2}$$

$$\xrightarrow[\Delta]{Br_2+NaOH} \underset{\text{Methylamine}}{CH_3NH_2} + 2NaBr + Na_2CO_3 + 2H_2O$$

(Hofmann bromamide reaction)

105. Give the structures of various amines with molecular formula C_3H_9N. State whether they are primary, secondary or tertiary amines?

ISC 2002

Ans :

Molecular formula of amine is C_3H_9N

(i) $\underset{\substack{\text{Ethyl methylamine}\\\text{(secondary)}}}{CH_3 - NH - CH_2CH_3}$

(ii) $\underset{\substack{\text{2-propanamine}\\\text{(primary)}}}{CH_3 - \underset{\displaystyle CH_3}{\underset{|}{CH}} - NH_2}$

(iii) $\underset{\substack{\text{Trimethylamine}\\\text{(tertiary)}}}{CH_3 - \underset{\displaystyle CH_3}{\underset{|}{N}} - CH_3}$

106. Write the balanced equations of the following reactions.

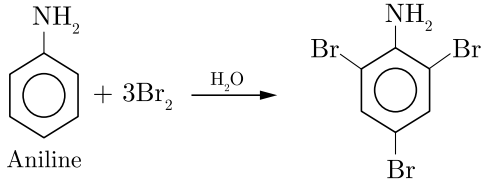
(i) Aniline and bromine water

(ii) Ethylamine and nitrous acid

(iii) Acetic anhydride and ammonia

ISC 2024

Ans :

(i) 

Aniline

2,4,6-tribromoaniline

(ii) $\underset{\text{Ethylamine}}{C_2H_5NH_2} + HNO_2 \longrightarrow \underset{\text{Ethanol}}{C_2H_5OH} + N_2\uparrow + H_2O$

(iii) $\underset{\text{Acetic anhydride}}{(CH_3CO)_2O} + NH_3 \longrightarrow \underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Acetamide}}{CH_3CONH_2}$

107. Identify the compounds $[A]$, $[B]$ and $[C]$ in the following reactions.

ISC 2023

(i) $CH_3COOH \xrightarrow[\Delta]{NH_3} [A] \xrightarrow{Br_2+KOH}$

$$[B] \xrightarrow{CHCl_3+NaOH(alc.)} [C]$$

(ii) $CH_3Br \xrightarrow{KCN} [A] \xrightarrow{LiAlH_4} [B] \xrightarrow[273\,K]{HNO_2} [C]$

Ans :

(i) $CH_3COOH \xrightarrow[\Delta]{NH_3} \underset{[A]}{CH_3CONH_2} \xrightarrow[273\,K]{HNO_2}$

$$\underset{[B]}{CH_3NH_2} \xrightarrow{CHCl_3+NaOH} \underset{[C]}{CH_3NC}$$

(ii) $CH_3Br \xrightarrow{KCN} \underset{[A]}{CH_3CN} \xrightarrow{LiAlH_4} \underset{[B]}{CH_3CH_2NH_2}$

$$\xrightarrow[273\,K]{HNO_2} \underset{[C]}{CH_3CH_2OH}$$

108. How can the following conversion be brought about

ISC 2022

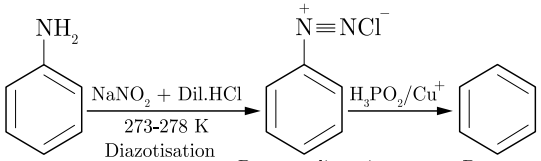
(i) acetic acid to methylamine ?

(ii) aniline to benzene ?

Ans :

(i) $\underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{NH_3} \underset{\text{Ammonium acetate}}{CH_3COO^-NH_4^+} \xrightarrow[-H_2O]{\Delta}$

$$\underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow{Br_2/KOH} \underset{\text{Methylamine}}{CH_3NH_2}$$

(ii) 

Aniline — Benzene diazonium chloride — Benzene

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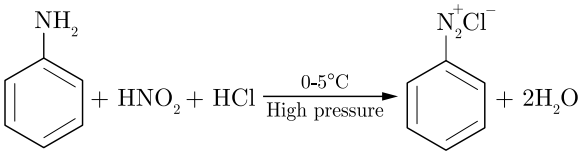
(ii) When aniline is treated with nitrous acid and HCl at 0-5°C temperature, then benzene diazonium salt is formed.



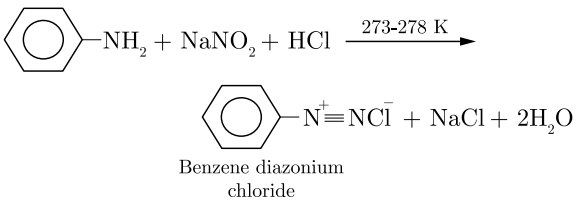
99. Give the chemical test to distinguish between the following pair of compounds.

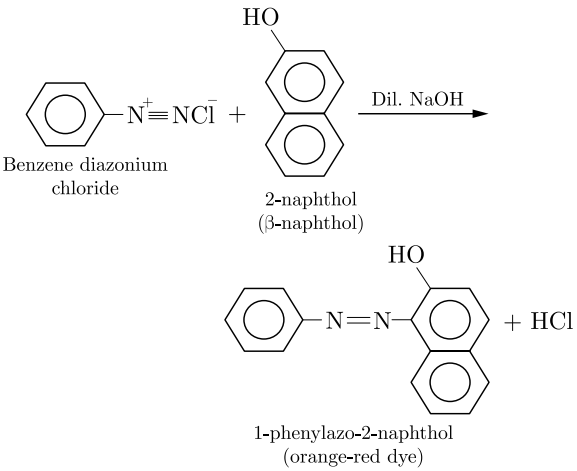
Aniline and ethylamine

ISC 2014

Ans :

Aniline and ethylamine are distinguished by azo-dye test which are as follows





Ethylamine does not form any dye and therefore, does not show any colour when treated with β -naphthol.

100. Identify compounds $[A]$ and $[B]$ in the following reactions.

ISC Specimen 2023

(i) $CH_3Br + KCN(alc.) \longrightarrow [A] \xrightarrow[\text{(Complete hydrolysis)}]{+HOH/H^+} [B]$

(ii) $C_6H_5NH_2 + HNO_2 + HCl \xrightarrow{0.5^\circ C} [A] \xrightarrow{Cu_2Cl_2/HCl} [B]$

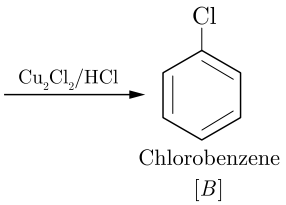
Ans :

(i) When an alkyl halide is heated with an alc. solution of KCN alkylcyanides are formed which on further hydrolysis carboxylic acid is obtained.

$$CH_3KCN(alc.) \xrightarrow{\Delta} \underset{(A)}{CH_3 - C \equiv N} + KX \xrightarrow{H_2O/H^+} \underset{(B)}{CH_3COOH}$$

(ii) When amide is treated with acid, diazonium salt is formed and on further treatment with copper chloride, the chlorobenzene is obtained.

$$\underset{\text{Aniline}}{C_6H_5NH_2} + \underset{\text{Nitric acid}}{HNO_2} + HCl \xrightarrow{0\text{-}5^\circ C} \underset{\text{Benzene diazonium chloride salt}}{C_6H_5N_2^+Cl^-}\ [A]$$



THREE MARKS QUESTIONS

101. How can the following conversion be brought about?

Benzene to acetanilide

ISC 2010

Ans :

Benzene to acetanilide

Following steps will be taken

$$\underset{\text{Benzene}}{C_6H_6} \xrightarrow[-H_2O]{HNO_3/H_2SO_4} \underset{\text{Nitrobenzene}}{C_6H_5NO_2} \xrightarrow[(Sn+HCl),-2H_2O]{4[H]} \underset{\text{Aniline}}{C_6H_5NH_2} \xrightarrow[-HCl]{CH_3COCl} \underset{\text{Acetanilide}}{C_6H_5NHCOCH_3}$$

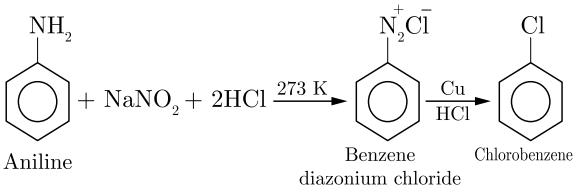
102. How will you carry out the following conversion?

Aniline to chlorobenzene.

ISC 2024

Ans :

Aniline to chlorobenzene



This reaction is known as diazotisation reaction.

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Reaction

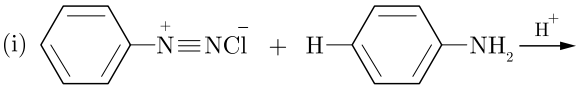
$$CH_3CONH_2 + Br_2 + 4KOH \longrightarrow CH_3NH_2 + 2KBr + K_2CO_3 + 2H_2O$$

Name of the reaction is Hofmann bromamide reaction.

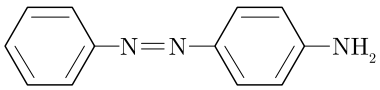
84. (i) What are the products formed when benzene diazonium chloride reacts with aniline in weakly acidic medium, at very low temperature? (Give equation)

ISC 2021-22 (Sem-II)

Ans :

(i) 

Benzene diazonium chloride Aniline

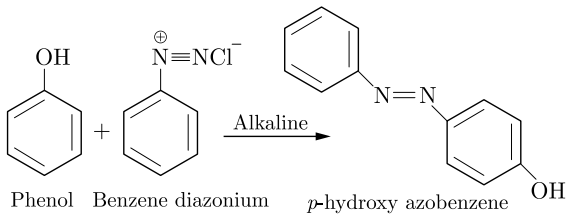


p-aminoazobenzene
(yellow dye)

85. What are the products formed when benzene diazonium chloride reacts with phenol in weak alkaline medium? (Give equation).

Ans : ISC Specimen 2021-22 (Sem-II

When benzene diazonium chloride reacts with phenol in weak alkaline medium results in the formation of *p*-hydroxy azobenzene.



Phenol Benzene diazonium salt *p*-hydroxy azobenzene

86. Identify the compounds *A*, *B*, *C* and *D*.

$$CH_3CN \xrightarrow{H_2O/H^+} [A] \xrightarrow{NH_3} [B] \xrightarrow{Heat} [C] \xrightarrow{Br_2/KOH} [D]$$

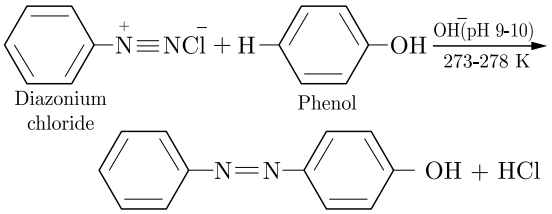
ISC 2018

Ans :

CH_3CN (Methyl cyanide) $\xrightarrow{H_2O/H^+}$ $CH_3COO^-H^+$ (Ethanoic acid (*A*)) $\xrightarrow{NH_3}$ CH_3COOH (Ammonium ethanoate (*B*)) $\xrightarrow{Heat}$ CH_3CONH_2 (Ethanamide (*C*)) $\xrightarrow[\text{Hofmann bromamide reaction}]{Br_2/KOH}$ CH_3NH_2 (Methylamine (*D*))

87. What happens when benzene diazonium chloride reacts with phenol in weak alkaline medium?(Give balanced equation).

Ans : ISC 2018



Diazonium chloride Phenol

p-hydroxy azobenzene
(Orange)

Benzene diazonium chloride reacts with phenol at its *para*-position to form *p*-hydroxy azobenzene, which is used as a dye.

88. Give balanced chemical equation for each of the following.

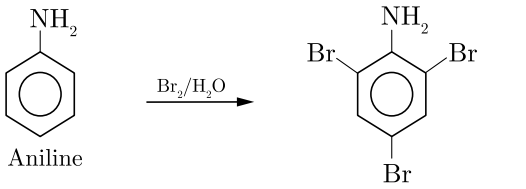
(i) Aniline and bromine water

(ii) Ethylamine and ethyl bromide

ISC 2021-22 (Sem-11), 2019

Ans :

(i)



Aniline 2,4,6-tribromoaniline

(ii) $\underset{\text{Ethylamine}}{CH_3CH_2-NH_2} + Br-CH_2CH_3 \xrightarrow{-HBr} \underset{\text{N, N – diethylamine}}{H_3C-CH_2-NH-CH_2CH_3}$

89. Arrange the following compounds in the ascending order of their basic strength and give reasons for your answer.

Methylamine, Aniline, Ethylamine, Diethyl ether

ISC 2015

Ans :

Basic strength order :

diethyl ether < aniline < methylamine < ethylamine

In aliphatic amines, due to the presence of electron donating alkyl group, electron density on nitrogen increases. Hence, lone pair is easily available for protonation.

NODIA

109. How can primary, secondary and tertiary aliphatic amines be distinguished by reaction with HNO_2 ($NaNO_2$ + Dil. H_2SO_4)?

ISC 2005

Ans :

Primary amines form alcohols with HNO_2.

$$RNH_2 + HONO \longrightarrow \underset{\text{Alcohol}}{R-OH} + N_2\uparrow + H_2O$$

Secondary amines form nitrosoamines with HNO_2

$$R_2NH + HONO \longrightarrow \underset{\text{Nitrosoamine}}{R_2N-N=O} + H_2O$$

Tertiary amines form trialkyl ammonium nitrite salt with HNO_2.

$$R_3N + HONO \longrightarrow \underset{\text{Trialkyl ammonium nitrite}}{R_3N\cdot HNO_2} \xrightarrow{\Delta}$$

$$\begin{array}{l} R \\ | \\ R-N-N=O \\ \text{N-nitrosoamine} \end{array} + \underset{\text{Alcohol}}{ROH}$$

110. Identify the compounds A, B, C, D, E and F required for the following conversion.

ISC 2014

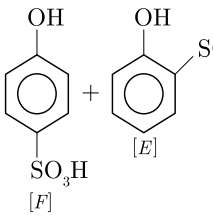
$$C_6H_5NO_2 \xrightarrow{[A]} C_6H_5NH_2 \xrightarrow{[B]} C_6H_5N_2^+Cl^- \xrightarrow{[C]}$$
$$C_6H_5Cl \xrightarrow{[D]} C_6H_5OH \xrightarrow{H_2SO_4} [E]+[F]$$

Ans :

$$C_6H_5NO_2 \xrightarrow[[A]]{Sn+HCl} C_6H_5NH_2 \xrightarrow[[B]]{NaNO_2+HCl} C_6H_5N_2^+Cl^-$$

$$C_6H_5N_2^+Cl^- \xrightarrow{Cu_2Cl_2/HCl} [C] \quad C_6H_5Cl$$

$$C_6H_5Cl \xrightarrow[[D]]{2NaOH + Dil.HCl} C_6H_5OH \xrightarrow{H_2SO_4}$$



111. Identify A, B and C.

ISC 2002

$$C_6H_5CONH_2 \xrightarrow{Br_2/KOH} [A] \xrightarrow[\text{(ii) Steam}]{\text{(i) } NaNO_2/HCl} [B]$$

$$\xrightarrow[\text{icc cold}]{C_6H_5N_2Cl} [C]$$

Ans :

$$C_6H_5CONH_2 \xrightarrow{Br_2/KOH} \underset{[A]}{C_6H_5NH_2} \xrightarrow{CHCl_3+KOH} \underset{[D]}{C_6H_5NC}$$

$$\xrightarrow[\text{(ii) Steam}]{\text{(i) } NaNO_2/HCl} \underset{[B]}{C_6H_5OH}$$

$$\underset{[E]}{CH_3COOC_6H_5} \xleftarrow{CH_3COOH} C_6H_5OH \xrightarrow[\text{Ice cold}]{C_6H_5N_2Cl}$$

$$\underset{\substack{p\text{-hydroxyazobenzene} \\ \text{(an azo dye)} \\ [C]}}{C_6H_5-N=N-C_6H_5OH}$$

112. How will the following be converted?

ISC 2023

(i) Ethyl bromide to ethyl isocyanide

(ii) Aniline to benzene diazonium chloride

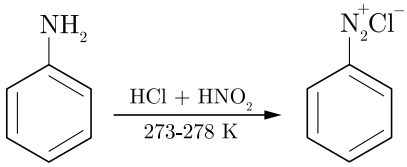
(iii) Benzene diazonium chloride to phenol

Ans :

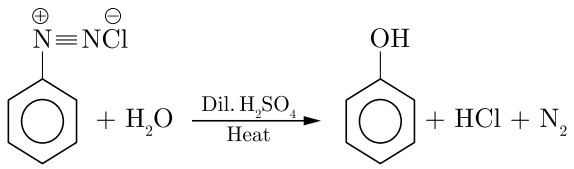
(i) Ethylbromide will react with alcoholic AgCN to give ethyl isocyanide (C_2H_5-NC)

$$C_2H_5-Br + AgCN \xrightarrow{\text{Aq. Et OH}} C_2H_5-NC + AgBr$$

(ii) When aniline reacts with dil. HCl and *aq.* solution of sodium nitrite ($NaNO_2$) at $273-278\,K$, it will form benzene diazonium chloride called diazotisation reaction.



(iii) When diazonium salts are hydrolysed in the presence of dil. H_2SO_4, its gives phenols.



113. An organic compound '*A*' on treatment with *aq.* KCN produces compound '*B*'. Compound '*B*' on reduction with Na/C_2H_5OH gives compound '*C* ' with molecular formula C_2H_5N. Compound '*C* ' reacts with $NaNO_2$ and HCl to form compound '*D*' on treatment with acetic acid in the presence of cone. H_2SO_4 produces a sweet smelling compound '*E* '.

ISC 2025

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Ans :
(i) Benzylamine.
(ii) No.
(iii) In benzylamine, the amino group is attached through a methylene group and therefore the lone pair on nitrogen does not participate in resonance with the benzene ring. In aniline, resonance delocalises the lone pair making it less available for protonation. Hence benzylamine is more basic than aniline.

140. A student treated methylamine and aniline separately with hydrochloric acid. Both compounds formed salts, but methylamine reacted more readily. The teacher explained that electron donating and resonance effects influence the basic nature of amines.
(i) Which amine reacted more readily with hydrochloric acid?
(ii) Which effect increases the basic strength of methylamine?
(iii) Explain why methylamine is more basic than aniline.

Ans :
(i) Methylamine.
(ii) Positive inductive effect.
(iii) The methyl group donates electron density towards nitrogen through positive inductive effect increasing availability of lone pair for protonation. In aniline, the lone pair participates in resonance with the benzene ring and becomes less available. Therefore methylamine behaves as a stronger base than aniline.

141. A chemist prepared aniline from nitrobenzene using tin and hydrochloric acid. After completion of the reaction, the solution was treated with sodium hydroxide to liberate free aniline. The teacher explained that reduction of nitro compounds is an important industrial method for preparation of aromatic amines.
(i) Which functional group is present in nitrobenzene?
(ii) Name the aromatic amine formed after reduction.
(iii) Explain why reduction of nitro compounds is important in organic chemistry.

Ans :
(i) Nitro group ($-NO_2$).
(ii) Aniline.
(iii) Reduction of nitro compounds provides an important method for preparation of aromatic amines. Aromatic amines such as aniline are widely used in manufacture of dyes, drugs, explosives and diazonium salts. The method is convenient because the nitro group can be selectively reduced without affecting the benzene ring.

142. During an organic conversion experiment, a student reacted methyl bromide with alcoholic potassium cyanide and obtained a nitrile compound. The nitrile was later reduced to form a primary amine containing one additional carbon atom.
(i) Which nitrile is formed from methyl bromide?
(ii) Which class of amines is obtained after reduction of nitriles?
(iii) Explain how this method helps increase carbon chain length.

Ans :
(i) Methyl cyanide.
(ii) Primary amines.
(iii) Cyanide ion introduces an additional carbon atom into the molecule during nucleophilic substitution. On reduction, the cyano group converts into amino group without loss of carbon atom. Therefore this method is important for preparation of higher primary amines with increased carbon chain length.

143. A student attempted diazotisation of aniline at room temperature and observed decomposition of the product with evolution of gas. The teacher explained the importance of temperature control during preparation of diazonium salts.
(i) Which gas is evolved during decomposition of diazonium salts?
(ii) At what temperature should diazotisation be carried out?
(iii) Explain why diazonium salts are unstable at higher temperatures.

Ans :
(i) Nitrogen gas.
(ii) 0–5°C
(iii) Diazonium salts possess weak diazonium linkage and therefore decompose easily at higher temperatures with liberation of nitrogen gas. The decomposition may occur violently in dry state. Hence diazonium salts are prepared and used immediately under cold conditions to maintain stability.

NODIA

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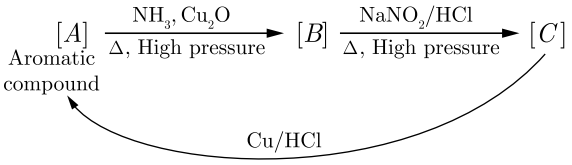
117. An aromatic organic compound $[A]$ on heating with NH_3 and Cu_2O at high pressure gives $[B]$. The compound $[B]$ on treatment with ice cold solution of $NaNO_2$ and HCl gives $[C]$ which on heating with Cu/HCl gives compound $[A]$ again. Identify the compounds $[A]$, $[B]$ and $[C]$. Write the name of the reaction for the conversion of $[B]$ to $[C]$.

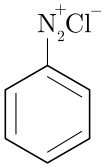
ISC 2018

Ans :

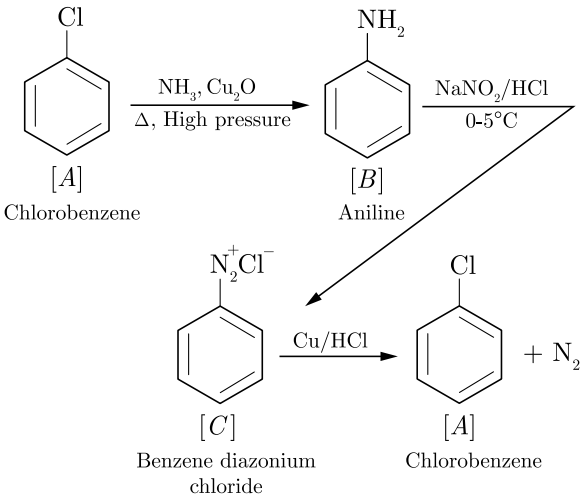
According to given information



The compound $[B]$ on treatment with ice cold solution of $NaNO_2$ and HCl gives $[C]$, which is most probably benzene diazonium chloride because compound $[A]$ is aromatic.

Compound $[C]$ is  which on

reaction with Cu/HCl forms compound $[A]$, i.e. chlorobenzene (Sandmeyer reaction)



118. Arrange the following as directed.

ISC 2009

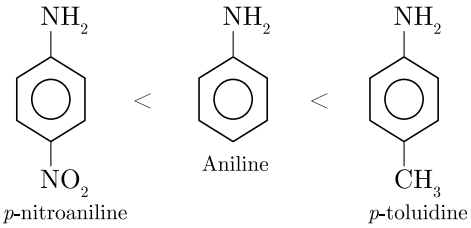
(i) Increasing order of basic strength. Aniline, *p*-nitroaniline and *p*-toluidine.

(ii) Decreasing order of basic strength in gas phase.
$C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$ and NH_3

(iii) Increasing order of solubility in water.
$C_6H_5NH_2$, $(C_2H_5)_2NH$, $C_2H_5NH_2$

Ans :

(i) Increasing order of basic strength is as follows



Reason More is the availability of electron density over N-atom, more is the basic strength. Electron releasing group increases while electron withdrawing group decreases the basicity (or basic strength).

(ii) Decreasing order of basic strength in gas phase is as follows

$(C_2H_5)_3N > (C_2H_5)_2NH > C_2H_5NH_2 > NH_3$

Reason Due to electron releasing nature of alkyl group, it pushes electron towards nitrogen and makes the unshared electron pair more available for sharing with the proton of the acid.
Basic nature of amine increases with increase in the number of alkyl group.

(iii) Increasing order of solubility of given compound in water is $C_6H_5NH_2 < (C_2H_5)_2NH < C_2H_5NH$

Reason Lower aliphatic amines can form hydrogen bonds with water molecule and hence are soluble in water.
Solubility of amines decreases with increase in molar mass due to increase in the hydrophobic part which retard the formation of H-bonds and hence aromatic amines are insoluble in water.

FOUR MARKS QUESTIONS

119. During an organic conversion experiment, a chemist converted ethanamide into methylamine using bromine and potassium hydroxide. Identify the reaction and explain why the product contains one carbon atom less than the reactant.

ISC 2003

Ans :

The reaction is Hofmann degradation reaction.

$$CH_3CONH_2 + Br_2 + 4KOH \rightarrow CH_3NH_2 + K_2CO_3 + 2KBr + 2H_2O$$

During the reaction, the carbonyl carbon of the amide group is removed in the form of carbonate ion.

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CHAPTER 10

Biomolecules

SUMMARY

1. BIOMOLECULES

Complex organic molecules which build up living organisms and are also required for their normal growth and development are called Biomolecules. They are formed inside the living cells and perform specific biological functions essential for the sustenance of life.

The important biomolecules found in living organisms are carbohydrates, amino acids, proteins, enzymes, nucleic acids, lipids, etc.

2. CARBOHYDRATES

Carbohydrates are one of the most abundant biomolecules in nature, serving as the primary source of energy and playing important structural roles in living organisms. Polyhydroxy aldehydes or ketones, or compounds that yield them on hydrolysis, are called carbohydrates or saccharides. They are of three types:

1. **Monosaccharides :** They are the simplest carbohydrates which cannot be hydrolysed into still simpler carbohydrates.
   Examples : Glucose ($C_6H_{12}O_6$), Fructose ($C_6H_{12}O_6$)
2. **Oligosaccharides :** They are the complex carbohydrates which can be hydrolysed into small number of monosaccharides.
   Example : Disaccharides : Sucrose, lactose, maltose ($C_{12}H_{22}O_{11}$)
   Trisaccharides : Raffinose ($C_{18}H_{32}O_{16}$)
   Tetrasaccharides : Stachyose ($C_{24}H_{42}O_{21}$) etc.
3. **Polysaccharides :** They are also the complex carbohydrates which can be hydrolysed into large number of monosaccharides.
   Example : Cellulose, starch, glycogen, etc.

2.1 Preparation of Glucose

Preparation of glucose are as follows :

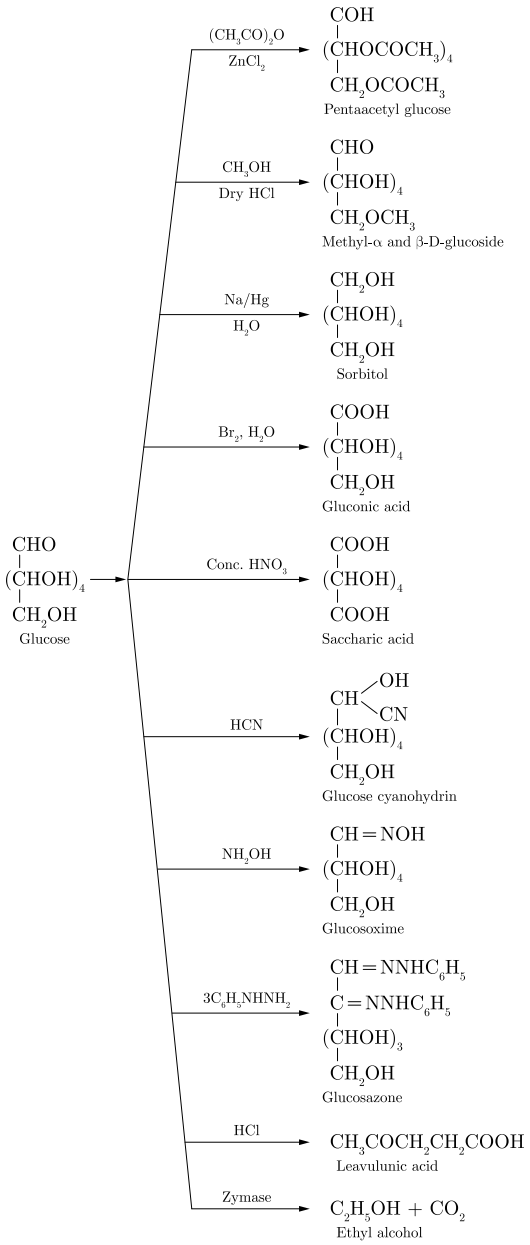
From Sucrose

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\Delta]{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

From Starch

$$(C_6H_{10}O_5)_n + nH_2O \xrightarrow[\Delta]{H^+} nC_6H_{12}O_6$$

2.2 Properties of Glucose



NODIA

126. A chemist compared the solubility of methylamine and aniline in water. Methylamine was highly soluble whereas aniline showed limited solubility. Explain the reason for this difference.

ISC 2012

Ans :

Lower aliphatic amines such as methylamine are soluble in water because they form hydrogen bonds with water molecules.

Aniline also forms hydrogen bonds but contains a large hydrophobic benzene ring.

The non-polar aromatic ring reduces interaction with water molecules.

Therefore aniline is only sparingly soluble compared to methylamine.

127. During preparation of propylamine from nitriles, ethyl cyanide was reduced using lithium aluminium hydride. Explain the reaction and state why the carbon chain length increases during this method.

ISC Specimen 2011

Ans :

Nitriles undergo reduction producing primary amines.

$C_2H_5CN \xrightarrow{LiAlH_4} C_3H_7NH_2$

The cyano group contains one carbon atom.

During reduction, this carbon atom becomes part of the alkyl chain of the amine.

Therefore reduction of nitriles is an important method for increasing carbon chain length during preparation of primary amines.

128. A student carried out the following reactions:

ISC Specimen 2023

1. Ethylamine reacted readily with hydrochloric acid forming a salt.
2. Aniline reacted less vigorously under similar conditions.

Based on these observations, explain why ethylamine is more basic than aniline. Also write the reactions involved.

Ans :

Ethylamine is more basic than aniline because in ethylamine the lone pair of electrons on nitrogen remains fully available for protonation.

In aniline, the lone pair is delocalised into the benzene ring due to resonance and becomes less available.

Reactions:

$C_2H_5NH_2 + HCl \rightarrow C_2H_5NH_3Cl$

$C_6H_5NH_2 + HCl \rightarrow C_6H_5NH_3Cl$

Thus ethylamine accepts proton more readily and behaves as a stronger base.

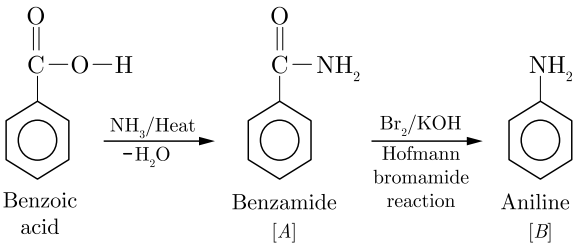
129. Identify A, B, C, D and E,

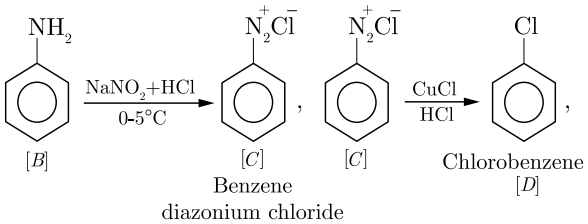
ISC 2001

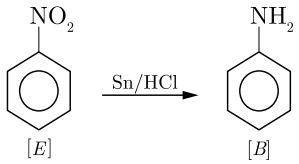
Benzoic acid $\xrightarrow[Heat]{NH_3}$ [A] $\xrightarrow{Br_2/KOH}$ [B]

[B] $\xrightarrow[Ice\ cold]{NaNO_2+HCl}$ [C] $\xrightarrow[HCl]{CuCl}$ [D]

Ans :







Since, E on reduction, gives aniline, hence it must be nitrobenzene, i.e. $C_6H_5NO_2$.

CASE BASED QUEATIONS

130. A student was comparing the basic strengths of ethylamine and aniline in the laboratory. It was observed that ethylamine reacted more readily with dilute hydrochloric acid than aniline. The teacher explained that resonance and inductive effects strongly influence the availability of lone pair of electrons on nitrogen atom in amines.

(i) Which amine is more basic?

(ii) Which effect decreases the basic strength of aniline?

(iii) Explain why ethylamine is more basic than aniline.

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(i) Identify the compounds 'A' to 'E'.

(ii) Name the reaction for the formation of compound 'E' from the compound 'D'.

Ans :

$$\underset{\text{Ethyl bromide}}{CH_3CH_2Br} \xrightarrow{Aq.\,KCN} \underset{\text{Ethyl cyanide}}{CH_3CH_2CN} \xrightarrow{Na/C_2H_5OH}$$

$$\underset{\text{Ethylamine}}{CH_3CH_2NH_2} \xrightarrow{NaNO_2+HCl} \underset{\text{Ethanol}}{CH_3CH_2-OH} \xrightarrow[\text{Conc.}H_2SO_4]{CH_3COOH} \underset{\substack{\text{Methyl ethyl ester}\\ \text{(Sweet smelling compound)}}}{CH_3CH_2COOCH_3}$$

(Ethylamine (C); Ethanol (D); (Esterification))

114. An organic compound $[A]$ with molecular formula C_2H_7N on reaction with nitrous acid gives a compound $[B]$. $[B]$ on controlled oxidation gives compound $[C]$. $[C]$ reduces Tollen's reagent to give silver mirror and $[D]$. $[B]$ reacts with $[D]$ in the presence of concentrated sulphuric acid to give sweet smelling compound $[E]$. Identify $[A]$, $[B]$, $[C]$, $[D]$ and $[E]$. Give the reaction of $[C]$ with ammonia.

ISC 2015

Ans :

$$\underset{[A]}{CH_3-CH_2-NH_2} + HNO_2 \longrightarrow \underset{[B]}{CH_3-CH_2-OH} + N_2\uparrow + H_2O$$

$$\underset{[B]}{CH_3-CH_2-OH} + [O] \xrightarrow[\text{Oxidation}]{\text{Controlled}} \underset{[C]}{CH_3-CHO} + H_2O$$

$$\underset{[C]}{CH_3-CHO} + 2[Ag(NH_3)_2]^+ + 3OH^- \xrightarrow{\Delta} \underset{[D]}{CH_3COOH} + 2Ag + 4NH_3 + 2H_2O$$

$$\underset{[D]}{CH_3COOH} + HO-\underset{[B]}{CH_2-CH_3} \overset{\text{Conc. } H_2SO_4}{\rightleftharpoons} \underset{\text{Ethyl acetate [E]}}{CH_3-COOC_2H_5} + H_2O$$

$$\underset{(C)}{CH_3-CHO} + NH_3 \longrightarrow CH_3-\underset{NH_2}{\overset{OH}{\underset{|}{\overset{|}{CH}}}} \xrightarrow{\Delta} CH_3-CH=NH$$

115. How will the following be converted ?
(Give chemical equations)

ISC Specimen 2023

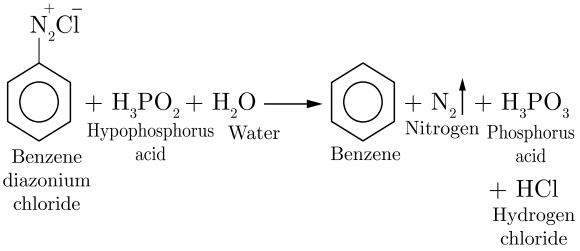
(i) Benzene diazonium chloride to benzene

(ii) Ethylamine to ethyl alcohol

(iii) Methylamine to methyl isocyanide

Ans :

(i) Benzene diazonium chloride to benzene



(ii) Ethylamine to ethyl alcohol

$$\underset{\text{Ethylamine}}{CH_3CH_2NH_2} \xrightarrow[0\text{-}5^\circ C]{NaNO_2 + HCl} CH_3CH_2\overset{+}{N}\equiv NCl^- \longrightarrow \overset{+}{C}H_3CH_2 \xrightarrow{\text{Hydrolysis}} \underset{\text{(Ethanol)}}{CH_3CH_2OH}$$

(iii) Methylamine to methyl isocyanide

$$\underset{\text{Methylamine}}{CH_3NH_2} + \underset{\text{Chloroform}}{CHCl_3} + 3KOH\,(\text{alc.}) \longrightarrow \underset{\substack{\text{Methyl}\\ \text{isocyanide}}}{CH_3NC} + \underset{\substack{\text{Potassium}\\ \text{chloride}}}{3KCl} + \underset{\text{Water}}{3H_2O}$$

It is an example of carbylamine reaction.

116. Identify the compounds A, B and C in the following reactions.

ISC Specimen 2023

(i) $C_6H_5NO_2 \xrightarrow{Sn+HCl} [A] \xrightarrow[273\,K-278\,K]{NaNO_2+HCl} [B] \xrightarrow{H_2O} [C]$

(ii) $CH_3CN \xrightarrow{H_2O/H^+} [A] \xrightarrow{NH_3/Heat} [B] \xrightarrow{Br_2+KOH} [C]$

Ans :

(i) $\underset{\text{Nitrobenzene}}{C_6H_5NO_2} \xrightarrow{Sn+HCl} C_6H_5NH_2 \xrightarrow[273\text{-}278\ K]{NaNO_2+HCl} \underset{\substack{\text{Benzene}\\ \text{diazonium}\\ \text{chloride } (B)}}{C_6H_5\overset{+}{N}_2Cl^-} \xrightarrow{H_2O} \underset{\substack{\text{Phenol}\\ (C)}}{C_6H_5OH}$

(ii) $\underset{\text{Acetonitrile}}{CH_3CN} \xrightarrow{H_2O/H^+} \underset{(A)}{CH_3CH_2OH} \xrightarrow[\text{Heat}]{NH_3/} \underset{\substack{\text{Ethanamide}\\ (B)}}{CH_3CONH_2} \xrightarrow{Br_2+KOH} \underset{\substack{\text{Methanamine}\\ (C)}}{CH_3NH_2}$

135. During a laboratory experiment, ethylamine and dimethylamine were separately treated with nitrous acid. Ethylamine produced brisk effervescence whereas dimethylamine formed a yellow oily liquid. The teacher explained that different classes of amines react differently with nitrous acid.

(i) Which gas is evolved when ethylamine reacts with nitrous acid?
(ii) What type of compound is formed by dimethylamine?
(iii) Explain how reaction with nitrous acid helps distinguish primary and secondary amines.

Ans :
(i) Nitrogen gas.
(ii) Nitrosoamine.
(iii) Primary aliphatic amines react with nitrous acid forming unstable diazonium salts which decompose immediately producing alcohol and nitrogen gas. Secondary amines react with nitrous acid forming yellow oily nitrosoamines. Therefore the different observations help distinguish between primary and secondary amines experimentally.

136. A student prepared propylamine by reducing ethyl cyanide using lithium aluminium hydride. The teacher explained that reduction of nitriles is an important method for increasing carbon chain length in organic synthesis.

(i) Which functional group is present in ethyl cyanide?
(ii) Which reducing agent is used in the reaction?
(iii) Explain why reduction of nitriles increases carbon chain length.

Ans :
(i) Cyano group ($-$ CN).
(ii) Lithium aluminium hydride ($LiAlH_4$).
(iii) The cyano group itself contains one carbon atom. During reduction, this carbon atom becomes part of the alkyl chain of the primary amine formed. Therefore reduction of nitriles provides an effective method for preparing amines having increased carbon chain length.

137. A chemist compared the boiling points of methane, methylamine and methanol. It was observed that methylamine had higher boiling point than methane but lower boiling point than methanol. The teacher related this trend to intermolecular forces present in the compounds.

(i) Which intermolecular force is present in methylamine?
(ii) Why does methanol have higher boiling point than methylamine?
(iii) Explain the trend in boiling points of methane, methylamine and methanol.

Ans :
(i) Hydrogen bonding.
(ii) Hydrogen bonding in alcohols is stronger.
(iii) Methane is non-polar and possesses only weak van der Waals forces. Methylamine forms intermolecular hydrogen bonds due to presence of N-H bond, increasing its boiling point. Methanol forms even stronger hydrogen bonding because oxygen is more electronegative than nitrogen. Therefore boiling point increases in the order:
$CH_4 < CH_3NH_2 < CH_3OH$

138. A laboratory assistant attempted acylation reactions using ethylamine and trimethylamine separately. Ethylamine produced an amide derivative whereas trimethylamine showed no reaction under identical conditions.

(i) Which class of amines undergoes acylation reactions?
(ii) Why does trimethylamine fail to undergo acylation?
(iii) Explain the importance of acylation reaction in identification of amines.

Ans :
(i) Primary and secondary amines.
(ii) It lacks hydrogen atom attached to nitrogen.
(iii) Acylation converts amines into stable amide derivatives having definite melting points. Primary and secondary amines undergo this reaction while tertiary amines do not. Therefore acylation reactions help distinguish tertiary amines from primary and secondary amines during qualitative organic analysis.

139. A student observed that benzylamine is more basic than aniline although both compounds contain benzene ring. The teacher explained that resonance and availability of lone pair electrons strongly influence the basic character of aromatic amines.

(i) Which compound is more basic?
(ii) Does resonance occur between amino group and benzene ring in benzylamine?
(iii) Explain why benzylamine is more basic than aniline.

NODIA

Therefore the amine formed contains one carbon atom less than the parent amide.

This reaction is important for preparation of lower primary amines.

120. A student treated ethylamine with chloroform and alcoholic potassium hydroxide. A foul smelling compound was produced immediately. Name the reaction and explain why only primary amines respond to this test.

ISC 2016

Ans :

The reaction is carbylamine reaction.

$C_2H_5NH_2 + CHCl_3 + 3KOH \rightarrow C_2H_5NC + 3KCl + 3H_2O$

Primary amines produce foul smelling isocyanides or carbylamines.

The reaction requires presence of hydrogen atoms attached to nitrogen atom.

Secondary and tertiary amines lack the required number of hydrogen atoms and therefore do not give this test.

121. A chemistry student prepared benzene diazonium chloride from aniline in the laboratory. Explain the preparation with balanced equation and state why the reaction temperature must be maintained between 0–5°C.

ISC Specimen 2011

Ans :

Aniline reacts with nitrous acid generated in situ from sodium nitrite and hydrochloric acid forming benzene diazonium chloride.

$C_6H_5NH_2 + NaNO_2 + 2HCl \rightarrow C_6H_5N_2Cl + NaCl + 2H_2O$

The reaction is carried out at 0–5°C because diazonium salts are stable only at low temperature.

At higher temperatures they decompose rapidly with liberation of nitrogen gas.

122. A chemist attempted acylation reactions using ethylamine and trimethylamine separately. Ethylamine reacted successfully whereas trimethylamine did not. Explain the observation with suitable equation.

ISC 2025

Ans :

Acylation reactions occur only in primary and secondary amines because they contain replaceable hydrogen atom attached to nitrogen.

Ethylamine reacts with acetyl chloride forming substituted amide.

$C_2H_5NH_2 + CH_3COCl \rightarrow CH_3CONHC_2H_5 + HCl$

Trimethylamine is a tertiary amine and lacks hydrogen attached to nitrogen.

Therefore it does not undergo acylation reaction.

123. A student added bromine water to aniline solution and observed formation of a white precipitate without using any catalyst. Explain the reaction and the role of amino group in this process.

ISC 2021

Ans :

Aniline reacts readily with bromine water producing white precipitate of 2,4,6-tribromoaniline.

$C_6H_5NH_2 + 3Br_2 \rightarrow C_6H_2Br_3NH_2 + 3HBr$

The amino group activates the benzene ring through resonance effect by donating electron density.

As a result electrophilic substitution occurs rapidly at ortho and para positions even without catalyst.

124. During reaction with nitrous acid, ethylamine produced brisk effervescence whereas dimethylamine formed a yellow oily compound. Explain both observations.

ISC 2013

Ans :

Primary aliphatic amines react with nitrous acid forming unstable diazonium salts which decompose immediately.

$C_2H_5NH_2 + HNO_2 \rightarrow C_2H_5OH + N_2 + H_2O$

Nitrogen gas is evolved vigorously.

Secondary amines react with nitrous acid forming yellow oily nitrosoamines.

Therefore the reactions help distinguish primary and secondary amines.

125. A student reduced nitrobenzene using tin and hydrochloric acid and obtained an aromatic amine. Explain the reaction and mention its importance in organic chemistry.

ISC 2024

Ans :

Nitrobenzene undergoes reduction forming aniline.

$C_6H_5NO_2 + 6[H] \rightarrow C_6H_5NH_2 + 2H_2O$

Reducing agents commonly used are tin and hydrochloric acid or iron and hydrochloric acid.

The reaction is important because aromatic amines prepared are widely used in manufacture of dyes, medicines and diazonium salts.

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144. A chemistry student compared ethylamine, dimethylamine and trimethylamine in aqueous solution and observed differences in their basic strengths. The teacher explained that both inductive effect and solvation influence the behaviour of amines in water.

(i) Which aliphatic amine is generally strongest base in aqueous solution?

(ii) Which effect increases electron density on nitrogen atom?

(iii) Explain why trimethylamine is not the strongest base despite having three alkyl groups.

Ans :

(i) Dimethylamine.

(ii) Positive inductive effect.

(iii) Although trimethylamine contains three electron donating alkyl groups, its protonated form is poorly solvated in aqueous solution because of steric hindrance. Dimethylamine experiences favourable balance between inductive effect and solvation. Therefore secondary amines are generally stronger bases than tertiary amines in water.

****

NODIA

Ans :
(i) Ethylamine.
(ii) Resonance effect.
(iii) In aniline, the lone pair of electrons on nitrogen participates in resonance with the benzene ring and becomes less available for protonation. In ethylamine, the lone pair remains localised and alkyl group exerts positive inductive effect increasing electron density on nitrogen. Therefore ethylamine behaves as a stronger base.

131. During an organic analysis experiment, a student treated ethylamine separately with chloroform and alcoholic potassium hydroxide. A foul smelling compound was produced immediately. However, dimethylamine and trimethylamine failed to produce the same observation.
(i) Name the reaction involved.
(ii) Which class of amines gives this test?
(iii) Why do secondary and tertiary amines fail to respond to this reaction?

Ans :
(i) Carbylamine reaction.
(ii) Primary amines.
(iii) Formation of isocyanides requires hydrogen atoms attached directly to nitrogen atom. Secondary amines contain only one hydrogen atom while tertiary amines contain no hydrogen atom attached to nitrogen. Therefore they cannot form the required intermediate and hence do not give carbylamine test.

132. A chemistry student prepared benzene diazonium chloride from aniline using sodium nitrite and hydrochloric acid at low temperature. The teacher warned students not to increase the temperature during the experiment because the product formed was thermally unstable.
(i) Name the process involved in the preparation of benzene diazonium chloride.
(ii) What temperature is maintained during the reaction?
(iii) Why must diazonium salts be prepared at low temperature?

Ans :
(i) Diazotisation.
(ii) 0–5°C.
(iii) Diazonium salts are stable only at low temperatures. At higher temperatures they decompose rapidly with liberation of nitrogen gas. Some dry diazonium salts may even explode violently. Therefore low temperature is essential during preparation and handling of diazonium compounds.

133. A chemist converted ethanamide into methylamine using bromine and potassium hydroxide. During the reaction, it was observed that the amine produced contained one carbon atom less than the parent amide. The teacher explained that this reaction is widely used for preparation of lower primary amines.
(i) Name the reaction involved.
(ii) Which reagent is responsible for bromination in the reaction?
(iii) Explain why the amine formed contains one carbon atom less than the parent amide.

Ans :
(i) Hofmann degradation reaction.
(ii) Bromine.
(iii) During Hofmann degradation, the carbonyl carbon of the amide group is removed in the form of carbonate ion. Therefore the resulting primary amine contains one carbon atom less than the parent amide. This reaction is useful for preparation of lower aliphatic and aromatic amines.

134. A student added bromine water to aniline solution and immediately observed formation of a white precipitate without using any catalyst. The chemistry teacher explained that the amino group strongly activates the benzene ring towards electrophilic substitution reactions.
(i) Identify the white precipitate formed.
(ii) Which positions of benzene ring are activated by amino group?
(iii) Explain why bromination of aniline occurs readily without catalyst.

Ans :
(i) 2,4,6-Tribromoaniline.
(ii) Ortho and para positions.
(iii) The amino group donates electron density into the benzene ring through resonance effect. This increases electron density particularly at ortho and para positions making the ring highly reactive towards electrophilic substitution. Therefore bromination occurs rapidly even in absence of Lewis acid catalyst.

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2.3 Mutarotation

The spontaneous change in specific rotation of an optically active compound with time until an equilibrium value is reached is called mutarotation.

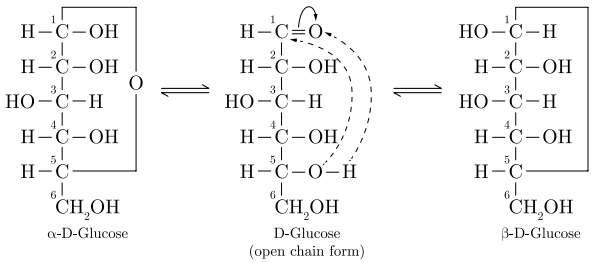
Example :

$$\underset{\text{Sp. rotation}\\ =+112^\circ}{\alpha-D-\text{glucose}} \rightleftharpoons \underset{\text{Sp. rotation}\\ =+52.5^\circ}{D-\text{glucose}} \rightleftharpoons \underset{\text{Sp. rotation}\\ =+19.2^\circ}{\beta-D-\text{glucose}}$$

2.4 Cyclic Structure of Glucose (Anomers)

Glucose has hemi-acetal structure in which C_5-OH of glucose combines with the C_1-CHO group. So C_1 becomes chiral C-atom due to which D-glucose exists in two forms.

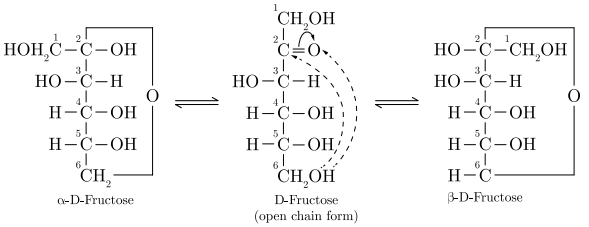
Structures I and II are the stereoisomers $\alpha = D$ D-glucose which differ in configuration only around C_1. They are called anomers of glucose and this C_1 carbon atom is called anomeric carbon atom.



2.5 Cyclic Structure of D-fructose

Fructose has hemi-ketal structure in which C_6-OH of fructose combines with C_2-CO group. So C_2 becomes chiral C-atom due to which D-fructose exists in two forms.

Structures I and II are the stereoisomers of D-fructose which differ in configuration only around C_2. They are called anomers of fructose and this C_2 atom is called anomeric carbon atom.



2.6 Disaccharides

Carbohydrates which on hydrolysis give two molecules (same or different) of monosaccharides are called disaccharides. The two monosaccharide units are joined together by a glycosidic bond formed by the elimination of a water molecule.

Example :

1. **Sucrose :**
$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$
2. **Maltose :**
$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Glucose}}{C_6H_{12}O_6}$$
3. **Lactose :**
$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Galactose}}{C_6H_{12}O_6}$$

NODIA

2.7 Invert Sugar

Sucrose is dextrorotatory. During the hydrolysis of sucrose, glucose and fructose are formed. The leavorotation of fructose is more than dextrorotation of glucose, so the mixture is leavorotatory. Such type of change in the rotation is called **inversion of sugar** and the mixture is called invert sugar.

2.8 Reducing Sugars

The carbohydrates which reduce Fehling's solution and Tollen's reagent are called reducing sugars. They contain free aldehydic $(-CHO)$ or ketonic $(>C=O)$ group with $-OH$ group on the carbon adjacent to carbonyl group.

Example : Maltose, lactose.

2.9 Non-reducing Sugars

The carbohydrates which do not reduce Fehling's solution and Tollen's reagent are called non-reducing sugars. They do not contain free aldehydic or ketonic group with $-OH$ group on the carbon adjacent to carbonyl group.

Example : Sucrose.

2.10 Starch

Starch is a polymer of D-glucose and is the most important food reserve carbohydrate in plants. It consists of two components :

1. **Amylose :** It is a linear polymer of D-glucose in which large number of D-(+)-glucose units are joined together by α-glycosidic linkage. It is soluble in water and gives blue colour with I_2.
2. **Amylopectin :** It is a branched chain polymer of D-glucose in which various D-(+)-glucose units are joined together by α-glycosidic linkages. It is insoluble in water and does not give blue colour with later.

Ans : (c) Primary structure

Denaturation disrupts secondary, tertiary and quaternary structures of proteins by breaking hydrogen bonds and other weak interactions. However peptide bonds remain intact and therefore the primary structure or amino acid sequence remains unchanged. Changes in temperature, pH or salts commonly cause denaturation of proteins.

21. A student observed that RNA contains uracil whereas DNA contains thymine. Which sugar is present in RNA?

ISC 2018

(a) Deoxyribose

(b) Ribose

(c) Glucose

(d) Fructose

Ans : (b) Ribose

RNA contains β-D-ribose sugar whereas DNA contains β-D-deoxyribose sugar. The presence of hydroxyl group at the second carbon atom distinguishes ribose from deoxyribose. RNA generally exists as single stranded molecule and plays important role in protein synthesis inside living cells.

22. Which process involves copying of DNA base sequence into RNA base sequence?

ISC 2020

(a) Translation

(b) Mutation

(c) Replication

(d) Transcription

Ans : (d) Transcription

Transcription is the process in which genetic information present in DNA is copied into messenger RNA molecule. RNA polymerase synthesises complementary RNA strand using DNA as template. The produced messenger RNA carries genetic code from nucleus to ribosomes where protein synthesis occurs during translation.

23. Which disaccharide is formed by combination of glucose and fructose units?

ISC 2018, 2008

(a) Maltose

(b) Lactose

(c) Sucrose

(d) Cellobiose

Ans : (c) Sucrose

Sucrose is a disaccharide composed of one glucose unit and one fructose unit linked through glycosidic bond. Because both anomeric carbon atoms participate in bond formation, sucrose behaves as non-reducing sugar. It is commonly obtained from sugar cane and sugar beet and serves as table sugar.

24. Which vitamin is also known as thiamine?

ISC 2018, 2008

(a) Vitamin B^1

(b) Vitamin B^2

(c) Vitamin B^{12}

(d) Vitamin E

Ans : (a) Vitamin B^1

Vitamin B^1 is chemically known as thiamine and is essential for proper functioning of nervous system and carbohydrate metabolism. Deficiency of thiamine causes beri-beri characterised by muscular weakness and nervous disorders. Rich dietary sources include milk, whole grains, yeast, nuts and green vegetables.

25. During hydrolysis of lactose, which pair of monosaccharides is produced?

ISC 2018

(a) Glucose and fructose

(b) Glucose and galactose

(c) Fructose and galactose

(d) Ribose and glucose

Ans : (b) Glucose and galactose

Lactose is a reducing disaccharide composed of glucose and galactose units joined through glycosidic linkage. On hydrolysis, the glycosidic bond breaks producing one molecule each of glucose and galactose. Lactose is commonly called milk sugar because it occurs naturally in milk and dairy products.

26. A student observed that boiling of egg changes the physical properties of protein permanently. Which phenomenon is responsible for this change?

ISC Specimen 2014

(a) Replication

(b) Mutarotation

(c) Denaturation

(d) Translation

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(ii) **β-Pleated Sheet Structure :** If alkyl group of α-amino acid is small, then this structure is formed.

It this structure, the peptide chains lie side by side in a zig-zag manner with alternate alkyl groups on the same side. These peptide chains are held together by H-bonds.

4.3 Denaturation of Proteins

A process that changes the physical and biological properties of proteins without changing the chemical composition of protein is called denaturation. It is caused by changes in pH, temperature, presence of salts etc.

The important features of denaturation of proteins are:

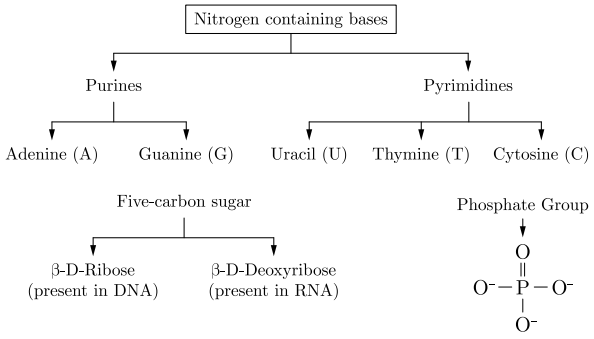
1. It does not change the primary structure but changes the secondary structure of protein.
2. It may or may not be reversible depending upon the nature of protein.
   Example : Coagulation of milk, boiling of egg.

5. NUCLEIC ACIDS

They are long chain polymers present in high concentration in the nucleus of the body cells.

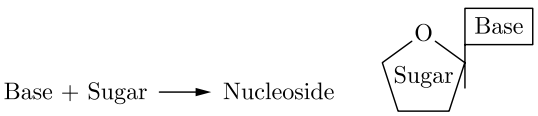
The repeating units of nucleic acids are called nucleotides. The nucleotides consist of three components:

1. A nitrogen containing base
2. A five carbon sugar
3. A phosphate group.



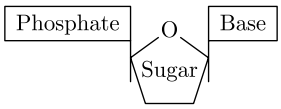
5.1 Nucleoside

It consists of nitrogen containing base and five carbon sugar.



5.2 Nucleotide

It consists of nitrogen containing base, five carbon sugar and phosphate unit.



Base + Sugar + Phosphate ⟶ Nucleotide

5.3 Distinguish between DNA and RNA

The difference between DNA and RNA are as follows:

	DNA	RNA
1.	β-D-Ribose sugar is present.	β-D-Deoxyribose sugar is present.
2.	It has (C), (T) as pyrimidine bases and (A), (G) as purines.	It has (C), (U) as pyrimidine bases and (A), (G) as purines.
3.	It has double α-helix structure.	It has single α-helix structure.
4.	It is present in nucleus of the cell.	It is present in cytoplasm of the cell.
5.	It can replicate.	It cannot replicate.
6.	It is responsible for hereditary characters.	It is responsible for protein synthesis.

NODIA

5.4 Replication

The process by which one DNA molecule makes two identical copies of itself is called replication. During this process, the hydrogen bonds between the complementary base pairs of the two strands of DNA break, allowing each strand to serve as a template for the synthesis of a new complementary strand.

5.5 Protein Synthesis

It occurs in two steps:

1. **Transcription :** The process of copying of DNA base sequence into a RNA base sequences is called transcription.

$$\underset{\text{Base sequence}}{\text{DNA}} \longrightarrow \text{A C T G}$$

$$\underset{\text{Base sequence}}{m\text{-RNA}} \longrightarrow \text{U G A C}$$

fibrous arrangement and extensive intermolecular bonding, keratin is insoluble in water and provides mechanical strength.

9. During hydrolysis of starch, the major monosaccharide obtained is:

ISC 2024

(a) Fructose

(b) Ribose

(c) Glucose

(d) Galactose

Ans : (c) Glucose

Starch is a polysaccharide composed entirely of D-glucose units linked through glycosidic bonds. Hydrolysis of starch breaks these linkages producing glucose molecules. Because of its abundant glucose content, starch acts as the major food reserve carbohydrate in plants and an important energy source for living organisms.

10. A student observed that amino acids migrate neither towards anode nor cathode at a particular pH. What is this pH called?

ISC 2018

(a) Neutral point

(b) Isoelectric point

(c) Saturation point

(d) Denaturation point

Ans : (b) Isoelectric point

Amino acids exist as zwitter ions containing both positive and negative charges. At a specific pH called isoelectric point, the net charge becomes zero and the amino acid does not migrate towards any electrode in an electric field. At this point amino acids generally show minimum solubility in water.

11. Which type of protein generally possesses thread-like structure and remains insoluble in water?

ISC Specimen 2023,

(a) Globular protein

(b) Fibrous protein

(c) Conjugated protein

(d) Derived protein

Ans : (b) Fibrous protein

Fibrous proteins consist of long thread-like polypeptide chains arranged side by side and stabilised by hydrogen bonding. They are generally insoluble in water and mainly perform structural functions. Examples include keratin in hair and collagen in connective tissues, both providing mechanical strength and support.

12. Which vitamin deficiency causes scurvy characterised by bleeding gums?

ISC 2025

(a) Vitamin A

(b) Vitamin D

(c) Vitamin C

(d) Vitamin K

Ans : (c) Vitamin C

Vitamin C or ascorbic acid is essential for proper collagen formation and maintenance of connective tissues. Deficiency of vitamin C causes scurvy characterised by bleeding gums, delayed wound healing and weakness. Citrus fruits such as oranges and lemons are important dietary sources of this vitamin.

13. Which statement correctly explains mutarotation in glucose?

ISC 2022, 2014

(a) Change in colour on heating

(b) Interconversion of α and β anomers in solution

(c) Hydrolysis into fructose

(d) Formation of peptide bond

Ans : (b) Interconversion of α and β anomers in solution

Mutarotation refers to the spontaneous change in optical rotation of glucose solution due to interconversion between α and β cyclic forms through open chain structure. As equilibrium establishes between the anomers, the specific rotation gradually changes until a constant equilibrium value is reached.

14. Which component is absent in nucleosides but present in nucleotides?

ISC 2022, 2014

(a) Nitrogenous base

(b) Pentose sugar

(c) Phosphate group

(d) Amino group

Ans : (c) Phosphate group

Nucleosides consist of nitrogenous base attached to pentose sugar. When a phosphate group

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3. The deficiency of vitamin D causes

ISC 2025

(a) rickets (b) gout

(c) scurvy (d) night blindness

Ans : (a) rickets

Vitamin D helps in the absorption of calcium and phosphorus, which are essential for healthy bones and teeth. Deficiency of vitamin D leads to weak and soft bones, causing a disease called rickets in children. Gout is related to uric acid, scurvy is caused by vitamin C deficiency, and night blindness is caused by vitamin A deficiency.

4. During qualitative analysis, a student treated glucose solution separately with Fehling's solution and Tollens' reagent. In both cases positive tests were observed. Which property of glucose is responsible for these reactions?

ISC 2021, 2012

(a) Presence of glycosidic bond

(b) Presence of free aldehydic group

(c) Presence of peptide bond

(d) Presence of ester linkage

Ans : (b) Presence of free aldehydic group

Glucose is a reducing sugar because it contains a free aldehydic group in its open chain structure. This aldehydic group reduces Fehling's solution to cuprous oxide and Tollens' reagent to metallic silver. Therefore glucose gives positive tests with both reagents and behaves as a reducing carbohydrate.

5. Which polysaccharide serves as the main structural component of plant cell walls?

ISC 2023

(a) Starch

(b) Glycogen

(c) Cellulose

(d) Maltose

Ans : (c) Cellulose

Cellulose is a linear polymer of β-D-glucose units joined through β-glycosidic linkages. Extensive hydrogen bonding between chains provides high tensile strength making cellulose the chief structural material of plant cell walls. Unlike starch, cellulose cannot be digested by humans because digestive enzymes cannot break β -glycosidic bonds.

6. A carbohydrate was found to reduce Fehling's solution and also showed mutarotation. Which carbohydrate among the following satisfies both conditions?

ISC 2021, 2011

(a) Sucrose

(b) Maltose

(c) Starch

(d) Cellulose

Ans : (b) Maltose

Maltose is a reducing disaccharide because one anomeric carbon remains free and can open into aldehydic form. It also exhibits mutarotation due to interconversion between α and β anomeric forms. Sucrose lacks free anomeric carbon and therefore neither shows reducing property nor mutarotation.

7. The pair of sugars which give the same product with excess of phenylhydrazine are

ISC 2002

(a) starch and cellulose

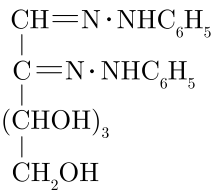
(b) cellulose and sucrose

(c) sucrose and glucose

(d) glucose and fructose

Ans : (d) glucose and fructose

Glucose and fructose both form same product (osazone) with excess of phenylhydrazine.



8. Which biomolecule acts as the primary structural material in hair, wool and nails?

ISC 2023, 2016

(a) Cellulose

(b) Keratin

(c) Glycogen

(d) Starch

Ans : (b) Keratin

Keratin is a fibrous protein possessing α-helix secondary structure stabilised by hydrogen bonds. It forms the major structural component of hair, nails, wool and feathers. Because of its

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Ans : (b) Replication

Replication is the process by which DNA makes identical copies of itself before cell division. Hydrogen bonds between complementary base pairs break and each strand acts as template for synthesis of a new complementary strand. Accurate replication ensures continuity of genetic information in living organisms.

33. A student identified a water-soluble vitamin deficiency disease as beri-beri. Which vitamin deficiency causes this disease?

ISC 2016

(a) Vitamin B^1

(b) Vitamin C

(c) Vitamin D

(d) Vitamin K

Ans : (a) Vitamin B^1

Beri-beri results from deficiency of vitamin B^1 or thiamine. This vitamin is essential for carbohydrate metabolism and proper functioning of nervous system. Deficiency leads to muscular weakness, fatigue and neurological disorders. Rich dietary sources include milk, rice, whole grains, nuts and yeast.

34. A student hydrolysed sucrose and observed that the resulting solution became levorotatory although sucrose itself is dextrorotatory. What is this phenomenon called?

ISC 2019, 2007

(a) Mutarotation

(b) Denaturation

(c) Inversion of sugar

(d) Replication

Ans : (c) Inversion of sugar

Sucrose hydrolyses into glucose and fructose. Although glucose is dextrorotatory, fructose is strongly levorotatory and its optical rotation dominates the mixture. Consequently the hydrolysed solution becomes levorotatory. This change in optical rotation from dextrorotation to levorotation is called inversion of sugar and the product is called invert sugar.

35. Assertion (A) : Glucose gives positive Tollens' test.

Reason (R) : Glucose contains free aldehydic group in its open chain structure.

ISC 2021, 2019

(a) Both A and R are true and R is the correct explanation of A

(b) Both A and R are true but R is not the correct explanation of A

(c) A is true but R is false

(d) A is false but R is true

Ans : (A) Both A and R are true and R is the correct explanation of A.

Glucose is a reducing sugar because it contains a free aldehydic group in its open chain structure. This aldehydic group reduces Tollens' reagent producing silver mirror. Therefore glucose gives positive Tollens' test and behaves as a reducing carbohydrate.

36. Assertion (A) : Sucrose is a non-reducing sugar.

Reason (R) : Both anomeric carbon atoms in sucrose are involved in glycosidic bond formation.

ISC 2022

(a) Both A and R are true but R is not the correct explanation of A

(b) Both A and R are true and R is the correct explanation of A

(c) A is true but R is false

(d) A is false but R is true

Ans : (B) Both A and R are true and R is the correct explanation of A.

In sucrose, the anomeric carbon atoms of glucose and fructose participate in glycosidic bond formation. Therefore no free aldehydic or ketonic group remains available for reduction reactions. Consequently sucrose does not reduce Fehling's solution or Tollens' reagent and behaves as non-reducing sugar.

37. Assertion (A) : Cellulose cannot be digested by humans.

Reason (R) : Human digestive enzymes cannot hydrolyse β-glycosidic linkages.

ISC 2023

(a) A is true but R is false

(b) Both A and R are false

(c) Both A and R are true and R is the correct explanation of A

(d) A is false but R is true

Ans : (C) Both A and R are true and R is the correct explanation of A.

NODIA

becomes attached to the nucleoside, the resulting compound is called nucleotide. Nucleotides act as repeating structural units of nucleic acids such as DNA and RNA which carry genetic information in living organisms.

15. During qualitative analysis, a student found that sucrose did not reduce Fehling's solution although it is a carbohydrate. What is the main reason for this behaviour?

ISC 2022, 2014

(a) Absence of hydroxyl groups

(b) Absence of free aldehydic or ketonic group

(c) Presence of peptide bond

(d) Presence of amino group

Ans : (b) Absence of free aldehydic or ketonic group

In sucrose, the anomeric carbon atoms of glucose and fructose are involved in glycosidic bond formation. Therefore no free aldehydic or ketonic group remains available for reduction reactions. Consequently sucrose fails to reduce Fehling's solution and Tollens' reagent and behaves as a non-reducing sugar.

16. A student compared amylose and amylopectin present in starch. Which component possesses branched chain structure?

ISC Specimen 2018

(a) Amylose

(b) Cellulose

(c) Amylopectin

(d) Glycogen

Ans : (c) Amylopectin

Amylopectin is a branched chain polysaccharide composed of D-glucose units joined mainly through α-1,4-glycosidic linkages with branching through α-1,6-linkages. Amylose, on the other hand, possesses linear structure. The branched arrangement in amylopectin contributes to the compact storage form of starch in plants.

17. Which amino acid property is responsible for its existence as zwitter ion in aqueous solution?

ISC 2018

(a) Presence of aromatic ring

(b) Presence of both amino and carboxyl groups

(c) Presence of peptide bond

(d) Presence of glycosidic linkage

Ans : (b) Presence of both amino and carboxyl groups

Amino acids contain both acidic carboxyl group and basic amino group in the same molecule. In aqueous solution, proton transfer occurs internally forming dipolar ions called zwitter ions. The amino group acquires positive charge while carboxyl group acquires negative charge making the molecule electrically neutral overall.

18. Which vitamin deficiency leads to rickets in children?

ISC 2018

(a) Vitamin C

(b) Vitamin B^1

(c) Vitamin D

(d) Vitamin K

Ans : (c) Vitamin D

Vitamin D plays an important role in calcium and phosphorus metabolism and proper bone formation. Deficiency of vitamin D in children causes rickets characterised by soft and weak bones leading to skeletal deformities. Exposure to sunlight and intake of milk, eggs and cod liver oil help prevent this disease.

19. Which level of protein structure represents the specific sequence of amino acids in a polypeptide chain?

ISC Specimen 2018

(a) Secondary structure

(b) Tertiary structure

(c) Quaternary structure

(d) Primary structure

Ans : (d) Primary structure

Primary structure of protein refers to the exact sequence in which amino acids are linked through peptide bonds in the polypeptide chain. Even slight alteration in amino acid sequence may significantly change biological function of the protein. This structure forms the basis for higher levels of protein organisation.

20. During denaturation of proteins, which structural level generally remains unaffected?

ISC 2018

(a) Secondary structure

(b) Tertiary structure

(c) Primary structure

(d) Quaternary structure

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2. **Translation :** The process in which m-RNA directs protein synthesis in the cytoplasm of cell with the involvement of t-RNA is called translation. Hence,

$$\text{DNA} \xrightarrow{\text{Replication}} \text{Two DNA strands}$$

$$\xrightarrow{\text{Transcription}} \text{Translation } m\text{-RNA}$$

$$\text{Protein} \longleftarrow t\text{-RNA, } r\text{-RNA}$$

5.6 Mutation

A chemical change in a DNA molecule that could lead to the synthesis of proteins with a different amino acid sequence is called mutation.

6. VITAMINS

Those biomolecules which are required in small amounts for normal growth and development of body are called vitamins. Their deficiency creates many diseases in the body. Vitamins are of two types.

1. **Water Soluble :** B_1, B_2, B_6, B_{12} and C are water soluble vitamins.
2. **Fat Soluble :** A, D, E, K are fat soluble vitamins.

Important Vitamins are :

Some important vitamins are as follows :

Vitamin	Chemical Name	Deficiency Disease	Sources of Vitamin
A	Retinal (bright eye vitamin)	Xerophthalmia i.e., hardening of cornea of eye, night blindness	Cod liver oil, shark liver oil, carrot, rice polishing, liver, kidney.
B1	Thiamine	Beri-Beri; disease of nervous system	Milk, rice, yeast, nuts, eggs, green vegetables.
B2	Riboflavin	Glossitis (dar red tongue), dermatitis and cheilosis (fissuring at corners of mouth and lips)	Turnip, milk, eggs, yeast, vegetables, liver, kidney.
B6	Pyridoxine	Dermatitis and convulsions	Meat, fish, egg yolk, whole cereal, grams.
B12	Cyanoco-balamin	Pernicious Anaemia, inflammation of tongue and mouth	Meat, eggs, liver of ox, sheep, pig, fish etc.
C	Ascorbic acid	Scurvy (bleeding of gums), pyorrhea	Citrus fruits like orange, lemon, tomato, green vegetables.
D	Ergocalciferol	Rickets and osteomalacia	Milk, eggs, cod liver oil
E	Tocopherol	Sterility	Oils like cotton seed oil, soyabean oil, wheat gram oil.
K	Phylloquinone	Haemophilia (haemorrhagic condition)	Cereals, leafy vegetables.
H	Biotin	Dermatitis, loss of hair and paralysis	Yeast, liver, kidney and milk.

OBJECTIVE QUESTIONS

1. Which of the following is an example of disaccharide?

(a) Glucose (b) Fructose

(c) Sucrose (d) Cellulose

ISC 2015

Ans : (c) Sucrose

Sucrose is a disaccharide formed by the combination of one molecule of glucose and one molecule of fructose. Glucose and fructose are monosaccharides, while cellulose is a polysaccharide. Therefore, sucrose is the correct example of a disaccharide.

2. Glucose on treatment with NH_2OH undergoes

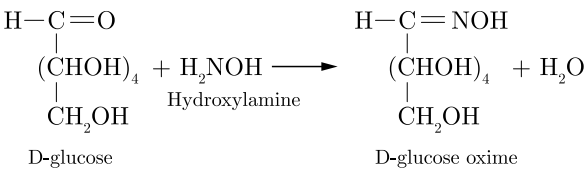
(a) condensation (b) reduction

(c) hydrolysis (d) oxidation

ISC 2004

Ans : (a) condensation

Glucose condenses with hydroxylamine to form an oxime called D-glucose oxime.



NODIA

Ans : (c) Denaturation

Denaturation involves alteration of secondary and tertiary structures of proteins due to heat, pH or chemicals without changing the primary structure. During boiling of egg, protein molecules unfold and coagulate irreversibly. As a result biological activity and original physical properties of proteins are lost permanently.

27. Which nitrogenous base is present in RNA but absent in DNA?

ISC 2023

(a) Adenine

(b) Cytosine

(c) Guanine

(d) Uracil

Ans : (d) Uracil

RNA contains uracil as pyrimidine base instead of thymine which occurs in DNA. Uracil pairs with adenine during RNA synthesis. This structural difference helps distinguish RNA from DNA. RNA mainly functions in protein synthesis whereas DNA stores and transmits hereditary genetic information.

28. Which polysaccharide gives blue colour with iodine solution?

ISC 2010

(a) Amylose

(b) Amylopectin

(c) Cellulose

(d) Glycogen

Ans : (a) Amylose

Amylose is a linear polymer of α-D-glucose units arranged in helical structure. Iodine molecules fit inside the helical cavity forming coloured complex which produces characteristic blue colour. Amylopectin and cellulose do not give the same intense blue colour because of their branched or different structural arrangements.

29. Which statement correctly explains the biological role of DNA?

ISC 2022

(a) DNA catalyses digestion reactions

(b) DNA stores and transmits hereditary information

(c) DNA acts as structural carbohydrate

(d) DNA supplies energy directly to cells

Ans : (b) DNA stores and transmits hereditary information

DNA contains genetic information encoded in sequence of nitrogenous bases. During replication, identical copies of DNA are produced ensuring transmission of hereditary characters from one generation to another. DNA also controls protein synthesis indirectly through transcription and translation processes occurring inside living cells.

30. Which amino acid category must be supplied through diet because the body cannot synthesise them?

ISC 2024, 2012

(a) Neutral amino acids

(b) Acidic amino acids

(c) Essential amino acids

(d) Non-essential amino acids

Ans : (c) Essential amino acids

Essential amino acids cannot be synthesised adequately by the human body and therefore must be obtained from food sources. They are necessary for growth, repair and protein synthesis. Deficiency of essential amino acids may impair normal physiological functions and development in living organisms.

31. Which type of bonding links amino acids together in proteins?

ISC 2024

(a) Glycosidic bond

(b) Hydrogen bond

(c) Peptide bond

(d) Phosphodiester bond

Ans : (c) Peptide bond

Amino acids join together through peptide bonds formed by condensation reaction between amino group of one amino acid and carboxyl group of another with elimination of water molecule. Repeated peptide bond formation produces polypeptide chains which fold into functional protein molecules.

32. Which process produces two identical DNA molecules from a parent DNA molecule?

ISC 2024, 2012

(a) Mutation

(b) Replication

(c) Translation

(d) Denaturation

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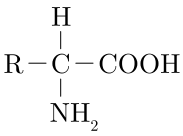
2.11 Cellulose

It is the main structural unit of plants. It is a linear polymer of D-glucose in which D-glucose units are joined by β-glycosidic linkage to form long chains which are held together by H-bonds.

3. AMINO ACIDS

α-Amino acids are the building blocks of proteins. They are organic compounds having both an amino group ($-NH_2$) and carboxylic group ($-COOH$) and represented as:



The amino acids are classified as acidic, basic or neutral depending upon the relative number of $-NH_2$ and $-COOCH$ groups in the molecules.

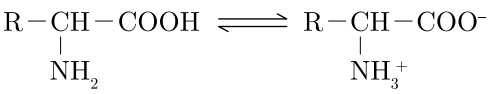
They are of two types:

1. **Non-essential Amino Acids :** These are the amino acids which can be made by our bodies and therefore, we do not require them in our diet. They are 10 in number.
   Examples : Glycine, alanine.
2. **Essential Amino Acids :** These are the amino acids which cannot be made by our bodies and must be supplied to our diet. They are also 10 in number. **Example :** Tyrosine, valine.

3.1 Properties of Amino Acids

The properties of amino acids are as follows:

1. Colourless, crystalline solids.
2. Soluble in water but insoluble in non-polar solvent.
3. In aqueous solution, an amino acid behaves like a dipolar ion called Zwitter ioin.



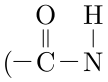
(Zwitter ion)

3.2 Isoelectric Point

The pH at which a particular amino acid does not migrate to any electrode under the influence of an electric field is called the Isoelectric Point.

At this point, amino acids have least solubility in water and this property is used for the separation of amino acid.

3.3 Peptides

They are the compounds formed by the condensation of two or more same or different α -amino acids. The resulting  linkage is called peptide bond.

4. PROTEINS

Proteins are large biological polymers of α-amino acids linked together by peptide bonds (–CO–NH–). They are the most abundant biomolecules in living cells and play a crucial role in almost all biological processes including catalysis, transport, structural support, and immune response..

4.1 Types of Proteins

They are of two types:

1. **Fibrous Proteins :** These types of proteins consist of linear thread like molecules which tend to lie side by side to form fibres. The molecules are held together by H-bonds. They are insoluble in water.
   Example : Keratin, Collagen.
2. **Globular Proteins :** In this type of proteins, the molecules are folded together into compact form. The peptide chains are held together by H-bonds. They are soluble in water.
   Example : Enzymes, hormones.

4.2 Structure of Proteins

Proteins exhibit four levels of structural organisation. The first two levels are as follows :

1. **Primary Structure :** It tells the sequence in which the various α-amino acids are present in the polypeptide chain.
   Each protein has a specific sequence of α -amino acids. If we change the sequence of any one α-amino acid, then the biological function of protein gets changed.
2. **Secondary Structure :** It gives the manner in which the polypeptide chains are folded or arranged. There are two types of secondary structures:
   (i) ***α*-Helix**
   Structure : If alkyl group of α-amino acid is large, then this structure is formed.
   In this structure, the peptide chains are coiled up to form a helix. The H-bonds are formed between $-CO$ group of one amino acid and $-NH$ group of other amino acid.
   Example : Keratin.

NODIA

Cellulose is composed of β-D-glucose units joined through β-glycosidic linkages. Human digestive system lacks the enzyme cellulase required for hydrolysis of these bonds. Therefore cellulose cannot be digested by humans although it serves as an important structural carbohydrate in plants.

38. Assertion (A) : Amino acids exist as zwitter ions in aqueous solution.
Reason (R) : Amino acids contain both acidic carboxyl group and basic amino group.
ISC Specimen 2017

(a) Both A and R are true and R is the correct explanation of A

(b) A is false but R is true

(c) Both A and R are true but R is not the correct explanation of A

(d) A is true but R is false

Ans : (A) Both A and R are true and R is the correct explanation of A.
Amino acids possess both amino group and carboxyl group in the same molecule. In aqueous solution, proton transfer occurs internally from carboxyl group to amino group forming dipolar ions called zwitter ions. Therefore amino acids exist predominantly as zwitter ions in aqueous medium.

39. Assertion (A) : Denaturation changes the primary structure of proteins.
Reason (R) : Denaturation breaks peptide bonds present in proteins.
ISC 2011

(a) Both A and R are false

(b) A is true but R is false

(c) A is false but R is true

(d) Both A and R are true and R is the correct explanation of A

Ans : (A) Both A and R are false.
Denaturation affects secondary and tertiary structures of proteins without changing the primary structure. Peptide bonds remain intact during denaturation. Only weak interactions such as hydrogen bonds are disrupted. Therefore the amino acid sequence of protein remains unchanged even after denaturation.

40. Assertion (A) : RNA contains uracil instead of thymine.
Reason (R) : RNA generally exists as single stranded molecule.
ISC 2024, 2012

(a) Both A and R are true but R is not the correct explanation of A

(b) A is false but R is true

(c) Both A and R are true and R is the correct explanation of A

(d) A is true but R is false

Ans : (A) Both A and R are true but R is not the correct explanation of A.
RNA contains uracil as pyrimidine base while DNA contains thymine. RNA is generally single stranded, but this structural feature does not explain the replacement of thymine by uracil. Both statements are correct independently but the reason does not correctly explain the assertion.

41. Assertion (A) : Amylose gives blue colour with iodine solution.
Reason (R) : Amylose possesses helical structure which traps iodine molecules.
ISC 2021

(a) Both A and R are true and R is the correct explanation of A

(b) Both A and R are true but R is not the correct explanation of A

(c) A is true but R is false

(d) A is false but R is true

Ans : (A) Both A and R are true and R is the correct explanation of A.
Amylose is a linear polymer of glucose arranged in helical form. Iodine molecules become trapped inside the helical cavity forming coloured complex which produces characteristic blue colour. Therefore iodine test is commonly used for identification of starch containing amylose component.

42. Assertion (A) : Essential amino acids must be supplied through diet.
Reason (R) : Human body cannot synthesise essential amino acids adequately.
ISC 2017, 2012

(a) A is true but R is false

(b) Both A and R are true and R is the correct explanation of A

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DIRECTION : Correct the following statement.

62. The base not present in DNA is guanine.
ISC 2002

Ans :
The base not present in DNA is uracil. In DNA thymine, instead of uracil, is found.

63. Glycine exists as a Zwitter ion at any pH
ISC 2000

Ans :
Glycine exists as a Zwitter ion at a particular pH known as isoelectric point.

64. Oxidation of sucrose with concentrated nitric acid yields glycerol.
ISC 2006

Ans :
Oxidation of sucrose with concentrated nitric acid yields oxalic acid.

65. How will you distinguish between glucose and sucrose?
ISC 2017

Ans :
With Tollen's reagent glucose give silver mirror test whereas sucrose does not.

66. A student observed that sucrose does not reduce Fehling's solution although it is a carbohydrate. State the type of sugar represented by sucrose.
ISC 2017, 2012

Ans :
Non-reducing sugar.

67. During hydrolysis of starch, which monosaccharide is obtained as the major product?
ISC 2024

Ans :
Glucose.]

68. Which structural feature of amino acids is responsible for the formation of zwitter ions in aqueous solution?
ISC 2022

Ans :
Presence of both amino $(-NH_2)$ and carboxyl $(-COOH)$ groups.

69. Name the biomolecule responsible for transmission of hereditary characters from one generation to another.
ISC 2015

Ans :
DNA.

70. Which component of starch gives blue colour with iodine solution?
ISC Specimen 2019, 2004

Ans :
Amylose.

71. Name the process in which the sequence of bases in DNA is copied into RNA.
ISC 2015, 2002

Ans :
Transcription.

72. Which vitamin deficiency disease is characterised by bleeding gums and delayed wound healing?
ISC Specimen 2025

Ans :
Scurvy.

73. Which type of protein structure is destroyed during denaturation without affecting amino acid sequence?
ISC 2011

Ans :
Secondary structure.

74. Name the bond responsible for linking monosaccharide units in disaccharides and polysaccharides.
ISC 2017, 2012

Ans :
Glycosidic bond.

75. Which nitrogenous base is present in RNA in place of thymine?
ISC 2011

Ans :
Uracil.

76. Which polysaccharide acts as the chief structural material of plant cell walls?
ISC 2010, 2005

Ans :
Cellulose.

NODIA

51. Which one of the following is a polysaccharide?
Starch, Maltose, Fructose and Glucose
ISC 2011

Ans :
Starch is a polysaccharide. It gives the large number α-D-glucose molecules on hydrolysis.

52. Name the two components of starch.
ISC 2008

Ans :
Starch is composed of amylose and amylopectin.

53. Which of the two components of starch is water soluble?
ISC 2025

Ans :
Starch consists of amylose and amylopectin. Among them amylose is a water soluble component of starch.

54. Which component of starch is a branched polymer of α-glucose and insoluble in water?
ISC 2018

Ans :
Amylopectin is a branched polymer of a-glucose and insoluble in water.

55. The deficiency of which vitamin will cause haemorrhage.
ISC 2014

Ans :
Deficiency of vitamin K causes haemorrhage. Vitamin K is obtained from leafy green vegetables.

56. What do you observe when glucose solution is heated with Tollen's reagent?
ISC 2016

Ans :
When glucose solution is heated with Tollen's reagent, silver mirror on the inner surface of the reaction vessel is observed.

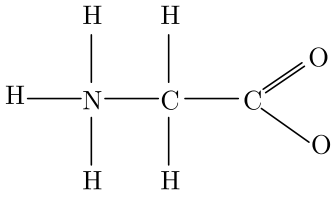
57. Give a test to distinguish between starch and cellulose.
ISC 2006

Ans :
To distinguish between starch and cellulose, iodine test is done starch converts yellow coloured iodine to blue black whereas cellulose does not.

NODIA

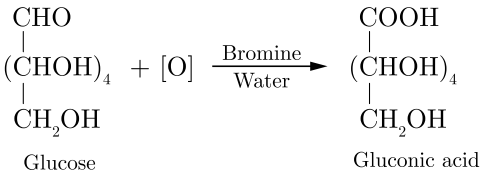
58. Write the Zwitter ion structure of glycine.
ISC 2024

Ans :
Zwitterionic structure of glycine can be given as follows :



59. How will you convert glucose to gluconic acid?
ISC 2003

Ans :
Glucose with bromine water form gluconic acid.



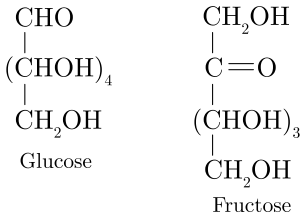
Glucose Gluconic acid

60. Classify the following into monosaccharides and disaccharides.
Ribose, 2-deoxyribose, Maltose, Galactose, Fructose and Lactose.
ISC 2021

Ans :
1. Monosaccharides : Ribose, 2-deoxyribose, galactose and fructose.
2. Disaccharides : Maltose and lactose.

61. Name the functional group common to both glucose and fructose.
ISC 2012

Ans :
Alcoholic (—OH) group is common in both, glucose and fructose.



Glucose Fructose

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + 9O_2 \xrightarrow{\text{Conc. } HNO_3} \underset{\text{Oxalic acid}}{6(COOH)_2} + 5H_2O$$

88. A nucleotide differs from a nucleoside by one component. Identify the component and state its importance.

ISC 2003

Ans :

The additional component is phosphate group.

Phosphate group links nucleotides together through phosphodiester bonds forming long chains of nucleic acids such as DNA and RNA.

89. Why is vitamin C considered essential in human diet? Mention one deficiency disease caused due to its deficiency.

ISC 2020

Ans :

Vitamin C is essential for collagen synthesis and maintenance of connective tissues.

Deficiency of vitamin C causes scurvy characterised by bleeding gums and delayed wound healing.

90. Why are essential amino acids called so? Give one example.

ISC 2020, 2016

Ans :

Essential amino acids are those which cannot be synthesised adequately by the human body and therefore must be supplied through diet.

Example : Valine.

91. What is isoelectric point of an amino acid? State its significance.

ISC 2013

Ans :

Isoelectric point is the pH at which amino acid carries no net electrical charge.

At this pH, amino acid does not migrate in electric field and shows minimum solubility in water.

92. Why is sucrose called invert sugar after hydrolysis?

ISC 2019

Ans :

Sucrose is dextrorotatory but on hydrolysis forms glucose and fructose. Fructose is strongly levorotatory causing overall solution to become levorotatory. This change in optical rotation is called inversion of sugar.

93. Explain the biological importance of carbohydrates in living organisms.

ISC 2023

Ans :

1. Carbohydrates act as the major source of energy for living organisms.
2. Structural carbohydrates such as cellulose provide rigidity and support in plant cell walls.

94. Name the purine bases and pyrimidine bases present in RNA and DNA.

ISC 2018

Ans :

Purine bases present in DNA and RNA are adenine (A) and guanine (G).

Pyrimidine bases present in DNA are thymine (T) and cytosine (C). Uracil (U) and cytosine (C) are present only in RNA.

95. Why do amino acids exist as zwitter ions in aqueous solution? Represent the zwitter ion form.

ISC 2024

Ans :

Amino acids contain both acidic carboxyl group and basic amino group. Internal transfer of proton forms zwitter ion.

Representation : $^{+}NH_3CH(R)COO^{-}$

96. Deficiency of what vitamins cause following disease.

(i) Night blindness

(ii) Scurvy

ISC 2017, 2014, 2011

Ans :

Deficiency of vitamin A causes night blindness and deficiency of vitamin C causes scurvy. Vitamin C is obtained from citrus fruits while the main sources of vitamin A are milk, fish, yellow ripe fruit and green vegetables.

97. Name the four bases present in DNA. Which one of these is not present in RNA?

ISC Specimen 2023

Ans :

The bases present used in DNA are adenine (A), cytosine (C), guanine (G) and thymine (T). In RNA, along with adenine (A), cytosine (C), guanine (G) and the base uracil (U) is presence in place of thymine.

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77. What is the name of the pH at which an amino acid carries no net electrical charge?
ISC Specimen 2010, 2005

Ans :
Isoelectric point.

78. Which category of amino acids must be supplied through diet because they cannot be synthesised by the body?
ISC 2008

Ans :
Essential amino acids.

79. Name the fibrous protein present in hair, nails and wool.
ISC 2020

Ans :
Keratin.

80. Which process produces two identical daughter DNA molecules from one parent DNA molecule?
ISC 2019

Ans :
Replication.

TWO MARKS QUESTIONS

81. Give an example each of reducing sugar and non-reducing sugar.
ISC 2023

Ans :
Glucose, fructose and ribose are reducing sugar. Sucrose and Raffinose are non-reducing sugar

82. Give an example each of water soluble vitamin and fat soluble vitamin.
ISC 2021

Ans :
Water soluble vitamin-vitamin C and B group vitamins. Fat soluble vitamins-These are vitamins A, D, E and K.

83. Deficiency of which vitamin causes the following diseases.
(a) Scurvy
(b) Night blindness
ISC 2015

Ans :
(a) Scurvy is caused due to deficiency to vitamin C.
(b) Night blindness is caused due to deficiency of vitamin A.

84. A carbohydrate on hydrolysis produced two molecules of glucose and reduced Tollens' reagent. Identify the carbohydrate and state why it behaves as a reducing sugar.
ISC 2008

Ans :
The carbohydrate is maltose.
Maltose behaves as a reducing sugar because one anomeric carbon atom remains free and can open into aldehydic form. Therefore it reduces Tollens' reagent and Fehling's solution.

85. A student observed that glucose solution gradually changed its optical rotation on standing. Name the phenomenon and explain its cause.
ISC 2021

Ans :
The phenomenon is mutarotation.
It occurs due to interconversion betweenα -D-glucose and β-D-glucose through open chain structure in aqueous solution until equilibrium is established.

86. Why does sucrose fail to give Fehling's test although glucose and fructose give positive result individually?
ISC 2020

Ans :
In sucrose, the anomeric carbon atoms of glucose and fructose are involved in glycosidic bond formation. Therefore no free aldehydic or ketonic group remains available for reduction. Hence sucrose does not give Fehling's test.

87. Name two water soluble vitamins and the diseases caused by their deficiency in the diet of an individual.
ISC 2019

Ans :
Vitamin-B and vitamin-C are water soluble and by the deficiency of vitamin-B and C in the diet beri-beri and scurvy diseases occurs, respectively.

NODIA

(c) Both A and R are true but R is not the correct explanation of A

(d) A is false but R is true

Ans : (B) Both A and R are true and R is the correct explanation of A.

Essential amino acids cannot be synthesised sufficiently by the human body and therefore must be obtained through food intake. These amino acids are necessary for protein synthesis, growth and normal physiological functions. Deficiency of essential amino acids may impair body development and metabolism.

43. Assertion (A) : DNA can replicate itself.
Reason (R) : DNA contains complementary base sequences.

ISC 2024, 2012

(a) Both A and R are true and R is the correct explanation of A

(b) Both A and R are false

(c) A is true but R is false

(d) A is false but R is true

Ans : (A) Both A and R are true and R is the correct explanation of A.

DNA strands possess complementary base pairing between adenine-thymine and guanine-cytosine. During replication, each strand acts as template for synthesis of new complementary strand. This complementary arrangement ensures accurate duplication of genetic information and formation of identical DNA molecules.

44. Assertion (A) : Vitamin C deficiency causes scurvy.
Reason (R) : Vitamin C is necessary for proper connective tissue formation.

ISC 2020

(a) Both A and R are true but R is not the correct explanation of A

(b) A is false but R is true

(c) Both A and R are true and R is the correct explanation of A

(d) A is true but R is false

Ans : (C) Both A and R are true and R is the correct explanation of A.

Vitamin C or ascorbic acid is essential for collagen synthesis and maintenance of connective tissues. Deficiency weakens connective tissues causing bleeding gums, delayed wound healing and scurvy. Therefore adequate intake of citrus fruits and vegetables is important to prevent vitamin C deficiency diseases.

FILL IN THE BLANK

45. Sucrose is a _____ and yields upon hydrolysis, a mixture of _____ and fructose.

ISC 2017

Ans :

Disaccharide, glucose

46. The base present in both DNA and RNA are _____ and _____.

ISC 2003

Ans :

The base present in both DNA and RNA are adenine and guanine.

47. Proteins are made up of _____ units held together by _____ linkages.

ISC 2004

Ans :

α-amino acid, peptide linkages

48. Proteins are _____ polymers of _____

ISC 2001

Ans :

Condensed, amino acid

ONE MARK QUESTIONS

49. What type of isomers glucose and fructose are?

ISC 2012

Ans :

Glucose and fructose are functional isomers.

50. Which one of the following is a disaccharide?
Starch, Maltose, Fructose and Glucose

ISC 2019

Ans :

Maltose is a disaccharide. It is composed of two α -D-glucose molecules.

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98. Explain why cellulose cannot be digested by human beings although starch can be digested easily.

ISC 2020

Ans :

Cellulose contains β-glycosidic linkages whereas starch contains α-glycosidic linkages. Human digestive enzymes can hydrolyse α-glycosidic bonds but cannot hydrolyse β-glycosidic bonds due to absence of cellulase enzyme.

99. A protein lost its biological activity when heated strongly but its peptide bonds remained unaffected. Name the process involved and state which structure of protein remains unchanged.

ISC 2025

Ans :

The process is denaturation.

The primary structure of protein remains unchanged because peptide bonds are not broken during denaturation.

100. Differentiate between fibrous proteins and globular proteins on the basis of structure and solubility.

ISC 2018

Ans :

Fibrous Proteins	**Globular Proteins**
Possess long thread-like structure.	Possess compact folded structure.
Generally insoluble in water.	Generally soluble in water.

101. State two important differences between DNA and RNA with respect to structure.

ISC 2021

Ans :

DNA	**RNA**
Contains deoxyribose sugar.	Contains ribose sugar.
Contains thymine.	Contains uracil.

102. A student added iodine solution to starch suspension and observed blue colour. Which component of starch is responsible for this observation and why?

ISC 2012

Ans :

Amylose is responsible for blue colour.

Amylose possesses helical structure in which iodine molecules get trapped forming coloured complex, producing characteristic blue colour.

103. Explain why amino acids are generally soluble in water but insoluble in non-polar solvents.

ISC 2021

Ans :

Amino acids exist as ionic zwitter ions in aqueous solution. These ions form strong ion-dipole interactions and hydrogen bonds with water molecules. Non-polar solvents cannot stabilise ionic species and therefore amino acids remain insoluble in them.

104. During replication, each DNA strand acts as template for formation of new strand. What feature of DNA makes this possible?

ISC 2015

Ans :

Complementary base pairing between nitrogenous bases makes replication possible.

Adenine pairs with thymine while guanine pairs with cytosine ensuring accurate synthesis of complementary strands.

105. Explain why globular proteins are generally more soluble in water than fibrous proteins.

ISC 2020, 2016

Ans :

Globular proteins possess compact folded structures exposing polar groups on the surface which interact readily with water molecules. Fibrous proteins mainly possess elongated structures with fewer exposed polar groups and therefore remain insoluble in water.

106. Explain why RNA is chemically less stable than DNA.

ISC 2021, 2012

Ans :

RNA contains ribose sugar having hydroxyl group at second carbon atom whereas DNA contains deoxyribose sugar lacking this hydroxyl group. Presence of additional hydroxyl group makes RNA more reactive and chemically less stable than DNA.

NODIA

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107. Write the two main functions of carbohydrate in plants.

ISC 2017, 2012

Ans :

Two main function of carbohydrate in plants are as follows :

(i) Carbohydrates are used as storage molecules like starch in plants.

(ii) Cell wall of bacteria and plants is made up of cellulose.

108. Carbohydrates are essential for life in both plants and animals.

ISC 2025

Name the carbohydrates that are used as storage molecules in plants and animals. Also, name the carbohydrate which is present in wood or in the fibre of cotton cloth.

Ans :

In plants, carbohydrates are stored in the form of starch while in animals, these are stored in the form of glycogen. Cellulose, a carbohydrate is present in wood or in the fibre of cotton cloth.

109. Write two differences between globular and fibrous proteins.

ISC 2017

Ans :

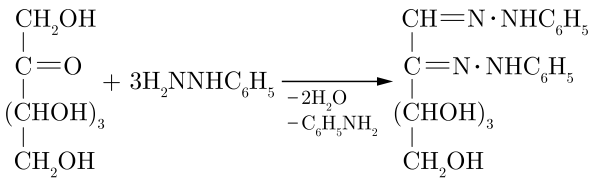
(i) **Fibrous proteins :** They have thread or fibre like structures in which polypeptide chains run parallel. These proteins are insoluble in water, e.g. keratin (found in hair, skin, nails, wool, silk) and myosin (present in muscles).

(ii) **Globular proteins :** They have spherical shape in which chains of polypeptides coil around. These are soluble in water, e.g. insulin and albumins.

110. Write relevant equation to convert fructose to Fructosazone.

ISC 2020

Ans :

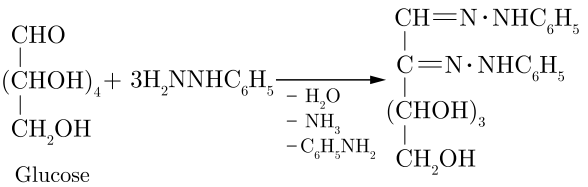


Fructose Fructosazone

111. How will you convert glucose to osazone?

ISC 2019

Ans :



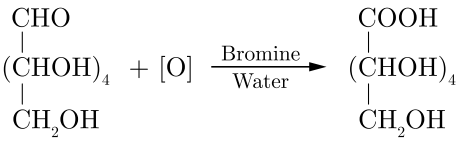
Glucose Glucosazone

112. Give one test to distinguish between glucose and fructose with relevant equation.

ISC 2017, 2012

Ans :

Glucose decolourises red colour of bromine water due to $-CHO$ group whereas fructose does not.



Glucose Gluconic acid

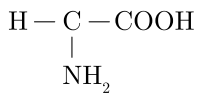
113. What is a Zwitter ion? Represent the Zwitter ion of glycine.

ISC Specimen 2021-22 (Sem-II)

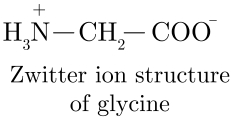
Ans :

The Zwitter ion is a molecule that equal number of positive and negative charged function group.

Structure of glycine



General formula of glycine



Zwitter ion structure of glycine

114. Differentiate between reducing and non-reducing sugars giving one example each.

ISC 2023, 2016

Ans :

Reducing Sugar	**Non-reducing Sugar**
Contains free aldehydic or ketonic group.	Does not contain free aldehydic or ketonic group.
Reduces Fehling's solution.	Does not reduce Fehling's solution.

Examples : Glucose and sucrose respectively.

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115. Give one example of fibrous protein. Name the final product of hydrolysis of proteins. What is denaturation of proteins?

ISC 2010, 2000

Ans :

Keratin is a fibrous protein. The final product of hydrolysis of a protein is a mixture of amino acids.

Change in physical and biological properties of a protein without affecting its chemical composition is called denaturation of proteins.

It may be caused by heating, reaction with alcohol, acid radiation etc. It changes only secondary and tertiary structures of proteins.

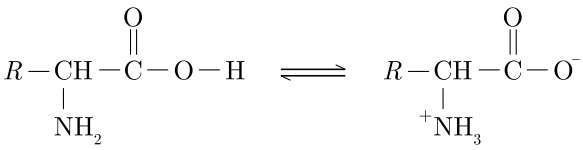
116. Explain the amphoteric behaviour of amino acids.

ISC 2018

Ans :

Amino acids contain both an acidic carboxyl group and a basic amino group.

In aqueous solution, they neutralise each other involving transfer of a proton from the carboxylic group to the amino group, giving rise to a dipolar ion known as 'Zwitter ion'. It is neutral but contains both positive and negative charges.



(Zwitter ion)

In Zwitter ionic form amino acids shows amphoteric behaviour as they can react with both acids and bases.

117. Answer the following questions.

(i) Give one example of an α-amino acid.

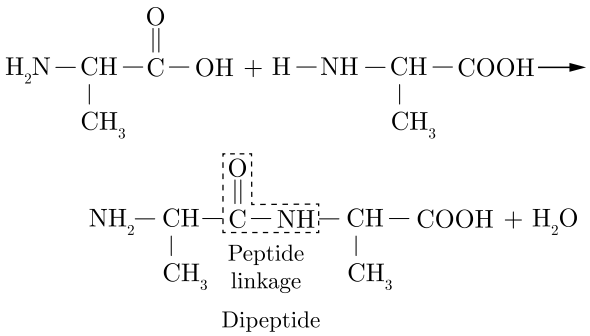
(ii) Write the structure of the dipeptide using this example.

ISC 2024

Ans :

(i) Alanine, $H_2N-\underset{\displaystyle CH_3}{\underset{|}{CH}}-COOH$

(ii) When two α-amino acids combine, a dipeptide is formed with the loss of a water molecule.



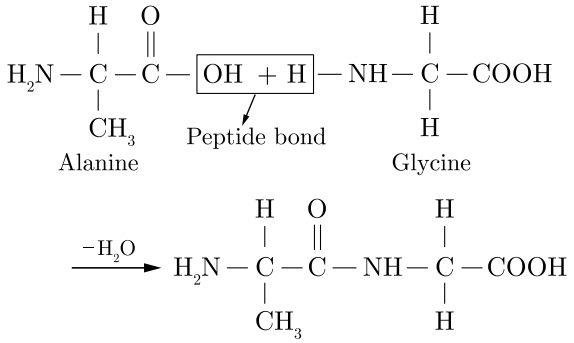
Dipeptide

118. What is peptide bond? Illustrate its formation with an example.

ISC 2021-22 (Sem-II)

Ans :

A peptide bond is a chemical bond that is formed by joining the carbonyl group of one amino acid to the amino group of other.



Alanine Peptide bond Glycine

NODIA

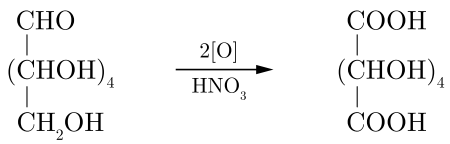
THREE MARKS QUESTIONS

119. How will you convert glucose to saccharic acid?

ISC 2009

Ans :

When glucose is oxidised with nitric acid, glucose yield a dicarboxylic acid known as saccharic acid.



Glucose Saccharic acid

120. What is isoelectric point of amino acids? Explain its importance in the separation of amino acids.
ISC 2019, 2007

Ans :

Isoelectric point is the pH at which amino acid carries no net electrical charge.

At this pH amino acid does not migrate in electric field.

Different amino acids possess different isoelectric points and therefore can be separated using electrophoresis technique.

121. Why is RNA considered chemically less stable than DNA?
ISC 2012

Ans :

RNA contains ribose sugar with hydroxyl group at second carbon atom whereas DNA contains deoxyribose lacking this hydroxyl group.

The additional hydroxyl group makes RNA more reactive and susceptible to hydrolysis.

Therefore RNA is chemically less stable than DNA.

122. Explain the role of vitamin C in human body and mention one deficiency disease caused by its deficiency.
ISC 2017

Ans :

Vitamin C is essential for collagen synthesis and maintenance of connective tissues.

It helps in wound healing and maintaining healthy gums.

Deficiency of vitamin C causes scurvy characterised by bleeding gums and delayed healing of wounds.

123. During an experiment, glucose solution showed gradual change in optical rotation until a constant value was attained. Name the phenomenon and explain the structural reason behind it.
ISC 2023, 2011

Ans :

The phenomenon is mutarotation.

In aqueous solution, glucose exists in equilibrium between:

$\alpha - D - glucose \rightleftharpoons$ Open chain form $\rightleftharpoons \beta - D - glucose$

Interconversion between the two cyclic forms through open chain structure changes the optical rotation gradually until equilibrium is established.

124. A student observed that DNA contains thymine while RNA contains uracil. State two additional structural differences between DNA and RNA.
ISC 2024

Ans :

DNA	**RNA**
Contains deoxyribose sugar.	Contains ribose sugar.
Usually double stranded.	Usually single stranded.

DNA mainly stores hereditary information while RNA participates in protein synthesis.

125. Why are essential amino acids necessary in human diet? Give any two examples.
ISC 2014

Ans :

Essential amino acids cannot be synthesised adequately by the human body and therefore must be obtained through diet.

They are necessary for growth, repair and protein synthesis.

Examples :

1. Valine
2. Leucine

126. Explain why amino acids are generally soluble in water but insoluble in non-polar solvents.
ISC 2021, 2012

Ans :

Amino acids exist as ionic zwitter ions in aqueous solution.

These ionic forms interact strongly with water molecules through ion-dipole attraction and hydrogen bonding.

Non-polar solvents cannot stabilise ionic species. Therefore amino acids remain insoluble in non-polar organic solvents.

127. During hydrolysis of lactose, two monosaccharides were formed. Identify them and explain why lactose behaves as a reducing sugar.
ISC 2024

Ans :

Lactose on hydrolysis forms:

1 Glucose

2 Galactose

Lactose behaves as a reducing sugar because one anomeric carbon atom remains free and can open into aldehydic form capable of reducing Fehling's solution and Tollens' reagent.

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128. Explain why amylose gives blue colour with iodine solution whereas cellulose does not show this behaviour.

ISC 2024

Ans :

Amylose possesses helical structure in which iodine molecules get trapped forming blue coloured complex.

Cellulose contains long straight chains with extensive hydrogen bonding and lacks helical arrangement.

Therefore cellulose does not trap iodine molecules and hence does not give blue colour with iodine solution.

129. A student compared starch and cellulose and observed that only starch could be digested by humans. Explain this observation on the basis of structure and bonding.

ISC 2021

Ans :

Starch contains α-glycosidic linkages between glucose units whereas cellulose contains β -glycosidic linkages.

Human digestive enzymes can hydrolyse α -glycosidic bonds but cannot hydrolyse β -glycosidic bonds due to absence of cellulase enzyme.

Therefore starch is digestible while cellulose is not digestible in humans.

130. Amino acids behave both as acids and bases in aqueous solution. Explain this behaviour with suitable representation.

ISC 2013, 2012

Ans :

Amino acids contain both acidic carboxyl group and basic amino group.

In aqueous solution they form zwitter ions:

$^{+}NH_3CH(R)COO^{-}$

The amino group can accept proton while the carboxyl group can donate proton. Therefore amino acids react with both acids and bases and show amphoteric behaviour.

131. A protein lost its biological activity when treated with concentrated acid, although peptide bonds remained unaffected. Name the process involved and explain the structural change responsible for loss of activity.

ISC 2022

Ans :

The process is denaturation of proteins.

Concentrated acid destroys secondary and tertiary structures by disrupting hydrogen bonds and weak intermolecular interactions.

As a result, protein loses its specific three-dimensional shape necessary for biological activity, although primary structure remains unchanged.

132. Differentiate between fibrous proteins and globular proteins giving one example of each.

ISC 2013, 2012

Ans :

Fibrous Proteins	**Globular Proteins**
Long thread-like structure.	Compact spherical structure.
Insoluble in water.	Soluble in water.
Mainly structural function.	Mainly biological and functional role.

Examples :

Keratin – fibrous protein

Haemoglobin – globular protein

133. Explain the biological importance of carbohydrates in plants and animals.

ISC 2017, 2012

Ans :

1 Carbohydrates act as major source of energy in animals.

2 Starch serves as storage carbohydrate in plants.

3 Cellulose provides structural strength to plant cell walls.

Thus carbohydrates perform both storage and structural functions in living organisms.

134. A nucleotide differs from a nucleoside in composition. Differentiate between the two and mention the linkage responsible for joining nucleotides in nucleic acids.

ISC 2025

Ans :

Nucleoside	**Nucleotide**
Contains sugar and nitrogenous base.	Contains sugar, nitrogenous base and phosphate group.

Nucleotides are joined together through phosphodiester linkage in nucleic acids.

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Ans :

(i) Glucose.

(ii) Cupric ions of Fehling's solution.

(iii) In sucrose, the anomeric carbon atoms of glucose and fructose are involved in glycosidic bond formation. Therefore no free aldehydic or ketonic group remains available for reduction. Hence sucrose behaves as a non-reducing sugar and fails to reduce Fehling's solution.

159. A researcher observed that RNA molecules degrade more rapidly than DNA molecules under similar conditions. The structural difference between the sugars present in DNA and RNA was identified as the major reason.

(i) Which sugar is present in RNA?

(ii) Which sugar is present in DNA?

(iii) Explain why RNA is chemically less stable than DNA.

Ans :

(i) Ribose sugar.

(ii) Deoxyribose sugar.

(iii) RNA contains ribose sugar having hydroxyl group at second carbon atom whereas DNA contains deoxyribose lacking this hydroxyl group. The additional hydroxyl group increases chemical reactivity and susceptibility to hydrolysis making RNA less stable than DNA.

160. A glucose solution was prepared in the laboratory and its optical rotation was measured immediately and after several hours. The value gradually changed and finally became constant. The chemistry teacher explained that cyclic forms of glucose continuously interconvert in aqueous solution.

(i) Name the phenomenon observed.

(ii) Which two cyclic forms are responsible for this behaviour?

(iii) Explain the structural basis of this phenomenon.

Ans :

(i) Mutarotation.

(ii) α-D-glucose and β-D-glucose.

(iii) In aqueous solution, the cyclic forms of glucose interconvert through open chain structure.

$\alpha - D - \text{glucose} \rightleftharpoons \text{Open chain} \rightleftharpoons \beta - D - \text{glucose}$

This continuous interconversion changes the optical rotation gradually until equilibrium is established.

161. A nutritionist advised an athlete to consume food rich in essential amino acids for proper muscle development. The athlete was informed that the human body cannot synthesise certain amino acids in sufficient quantity.

(i) What are such amino acids called?

(ii) Name any one essential amino acid.

(iii) Explain why essential amino acids must be included in diet.

Ans :

(i) Essential amino acids.

(ii) Valine.

(iii) Essential amino acids cannot be synthesised adequately by the human body. They are necessary for growth, repair of tissues and synthesis of proteins and enzymes. Therefore they must be obtained through food intake to maintain proper physiological activities.

162. A student compared DNA and RNA samples isolated from cells. It was observed that one sample contained thymine while the other contained uracil. The teacher explained that both nucleic acids differ in sugar component and biological role.

(i) Which nucleic acid contains uracil?

(ii) Which sugar is present in DNA?

(iii) State two structural differences between DNA and RNA.

Ans :

(i) RNA.

(ii) Deoxyribose sugar.

(iii)

DNA	**RNA**
Contains deoxyribose sugar.	Contains ribose sugar.
Usually double stranded.	Usually single stranded.

DNA stores hereditary information whereas RNA participates in protein synthesis.

163. A doctor advised a patient suffering from scurvy to increase intake of citrus fruits. Another patient suffering from weak and soft bones was advised exposure to sunlight and vitamin supplements. The doctor explained that vitamins regulate important physiological functions in the body.

(i) Deficiency of which vitamin causes scurvy?

(ii) Which vitamin deficiency causes rickets?

(iii) State one important function each of vitamin C and vitamin D.

NODIA

component 15-20%) and amylopectin (water insoluble component 80-85%).

Amylose is a linear polymer of α-D-glucose, while amylopectin is a highly branched polymers of α -D-glucose. Thus, both glycogen and amylopectin are branched chain condensation polymer of α -D-glucose.

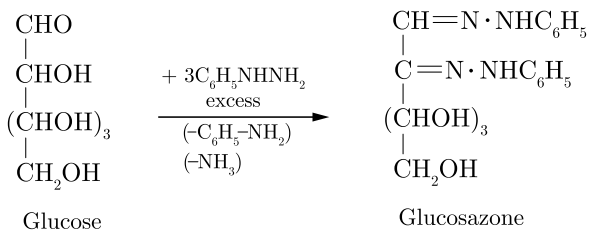
The only difference is that amylopectin chain consists of 20-25 glucose units whereas glycogen chain consists of 10-14 glucose units

142. How will you chemically convert glucose to fructose?

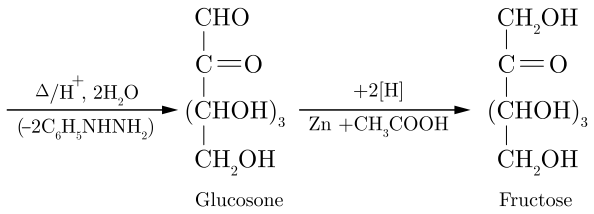
ISC 2001

Ans :

The reaction that convert glucose into fructose is



Glucose Glucosazone



Glucosone Fructose

FOUR MARKS QUESTIONS

143. Describe the biological importance of carbohydrates in living organisms.

ISC 2025

Ans :

1 Carbohydrates serve as major source of energy.

2 Glucose is essential for cellular respiration.

3 Starch acts as storage carbohydrate in plants.

4 Cellulose provides structural support to plant cell walls.

Some carbohydrates also participate in formation of nucleic acids and cell membranes.

144. Explain mutarotation in glucose. Why does this phenomenon occur only in reducing sugars?

ISC 2014, 2002

Ans :

Mutarotation is the spontaneous change in optical rotation of glucose solution on standing.

It occurs due to interconversion between:

$\alpha - \mathrm{D} - \mathrm{glucose} \rightleftharpoons$ Open chain form $\rightleftharpoons \beta - \mathrm{D} - \mathrm{glucose}$

through open chain structure.

Reducing sugars show mutarotation because they possess free anomeric carbon capable of opening into open chain form. Non-reducing sugars lack free anomeric carbon and therefore do not show mutarotation.

145. Compare starch and cellulose on the basis of structure, bonding and biological role.

ISC 2002

Ans :

Starch Cellulose

Contains α-glycosidic linkages.	**Contains β-glycosidic linkages.**
Helical structure.	Linear fibrous structure.
Digestible by humans.	Indigestible by humans.
Storage carbohydrate in plants.	Structural material of plant cell walls.

Human digestive enzymes hydrolyse α-glycosidic bonds but cannot hydrolyse β-glycosidic bonds due to absence of cellulase enzyme.

146. Explain the amphoteric nature of amino acids. What is meant by isoelectric point?

ISC 2014, 2002

Ans :

Amino acids contain:

1 Acidic carboxyl group $(-\mathrm{COOH})$

2 Basic amino group $(-\mathrm{NH_2})$

In aqueous solution they exist as zwitter ions:

$^{+}\mathrm{NH_3CH(R)COO^{-}}$

They react with acids through amino group and with bases through carboxyl group and therefore show amphoteric behaviour.

Isoelectric point is the pH at which amino acid carries no net electrical charge and does not migrate in electric field.

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153. What is replication of DNA? Explain the importance of complementary base pairing in this process.

ISC 2013

Ans :

Replication is the process in which DNA forms identical copies of itself before cell division.

Complementary base pairing occurs as:

$A - T$

$G - C$

Each parental strand acts as template for synthesis of complementary strand ensuring accurate duplication of genetic information and hereditary continuity.

154. Explain the difference between fibrous proteins and globular proteins with suitable examples and functions.

ISC 2017, 2012

Ans :

Fibrous Proteins	**Globular Proteins**
Long thread-like structure.	Compact spherical structure.
Insoluble in water.	Soluble in water.
Structural function.	Functional and metabolic role.

Examples :

1 Keratin – fibrous protein

2 Haemoglobin – globular protein

Fibrous proteins provide support whereas globular proteins function as enzymes and hormones.

155. Why are vitamins essential for human health although required in very small amounts? Discuss the deficiency diseases caused by vitamin C and vitamin D.

ISC 2020

Ans :

Vitamins regulate metabolic activities and act mainly as coenzymes in biochemical reactions. Therefore they are required only in small quantities.

Deficiency diseases:

1 Vitamin C deficiency causes scurvy characterised by bleeding gums.

2 Vitamin D deficiency causes rickets characterised by weak and soft bones.

156. A student observed that RNA is chemically less stable than DNA. Explain the structural reason for this difference.

ISC 2020

Ans :

RNA contains ribose sugar having hydroxyl group at second carbon atom whereas DNA contains deoxyribose sugar lacking this hydroxyl group.

The additional hydroxyl group in RNA increases chemical reactivity and susceptibility to hydrolysis.

Therefore RNA is chemically less stable than DNA and usually exists for shorter duration inside cells.

157. A student treated glucose separately with Fehling's solution and Tollens' reagent and observed positive results in both cases. Explain the structural basis of these reactions. Why does sucrose fail to give similar tests?

ISC 2013

Ans :

Glucose contains free aldehydic group in its open chain structure and therefore behaves as a reducing sugar.

It reduces:

1 Fehling's solution forming red precipitate of Cu_2O

2 Tollens' reagent producing silver mirror

Sucrose does not give these tests because the anomeric carbon atoms of glucose and fructose are involved in glycosidic bond formation. Therefore no free aldehydic or ketonic group remains available for reduction reactions.

CASE BASED QUEATIONS

158. A student performed Fehling's test separately with glucose and sucrose solutions. Glucose produced a brick-red precipitate whereas sucrose showed no visible change. The teacher explained that the difference arises due to the availability of free aldehydic or ketonic group in the carbohydrate molecules.

(i) Which carbohydrate behaved as a reducing sugar?

(ii) Which reagent is reduced during Fehling's test?

(iii) Explain why sucrose does not give Fehling's test.

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147. A protein lost its biological activity when heated strongly. Explain the process involved and discuss the structural changes taking place during the process.

ISC 2024

Ans :

The process is denaturation of proteins.

Heat disrupts:

1 Hydrogen bonds

2 Weak intermolecular interactions

responsible for secondary and tertiary structures of proteins.

As a result, the protein loses its specific three-dimensional shape and biological activity.

However peptide bonds remain intact and therefore primary structure remains unchanged during denaturation.

148. Differentiate between DNA and RNA on the basis of structure and biological functions.

ISC 2021, 2012

Ans :

DNA	**RNA**
Contains deoxyribose sugar.	Contains ribose sugar.
Contains thymine.	Contains uracil.
Usually double stranded.	Usually single stranded.
Stores hereditary information.	Participates in protein synthesis.

DNA controls inheritance whereas RNA plays role in transcription and translation.

149. Explain why cellulose acts as structural material in plants while starch acts mainly as storage carbohydrate.

ISC 2019

Ans :

Cellulose possesses long straight chains of glucose joined through β-glycosidic linkages. Extensive hydrogen bonding between chains provides rigidity and tensile strength making cellulose suitable for structural role in plant cell walls.

Starch possesses compact helical structure formed by α-glycosidic linkages suitable for storage of glucose units. Therefore starch acts mainly as storage carbohydrate.

150. What are nucleotides? Explain the structure of a nucleotide and the linkage responsible for formation of nucleic acids.

ISC 2019, 2003

Ans :

Nucleotides are the repeating structural units of nucleic acids.

Each nucleotide contains:

1 Nitrogenous base

2 Pentose sugar

3 Phosphate group

Nucleotides are linked through phosphodiester linkage formed between phosphate group of one nucleotide and sugar molecule of another nucleotide forming long DNA or RNA chains.

151. Explain why amino acids are soluble in water but insoluble in non-polar solvents.

ISC 2011, 2003

Ans :

Amino acids exist as zwitter ions in aqueous solution:

$^{+}NH_3CH(R)COO^{-}$

These ionic species form strong:

1 Ion-dipole interactions

2 Hydrogen bonds

with water molecules making them soluble in water.

Non-polar solvents cannot stabilise ionic species and therefore amino acids remain insoluble in non-polar organic solvents.

152. Explain the structural basis of reducing and non-reducing sugars with suitable examples.

ISC 2019

Ans :

Reducing sugars possess free aldehydic or ketonic group capable of reducing Fehling's solution and Tollens' reagent.

Examples :

1 Glucose

2 Maltose

Non-reducing sugars lack free aldehydic or ketonic group because reactive groups are involved in glycosidic bond formation.

Example :

Sucrose

Therefore non-reducing sugars do not give reduction reactions.

NODIA

Ans :

(i) Vitamin C.

(ii) Vitamin D.

(iii) Functions: :

1. Vitamin C: Required for collagen synthesis and maintenance of connective tissues.
2. Vitamin D : Required for absorption of calcium and proper bone formation.

164. A laboratory assistant added iodine solution separately to starch and cellulose suspensions. Starch produced deep blue colour while cellulose showed no colour change. The teacher explained that structural arrangement of glucose units determines the result of iodine test.

(i) Which component of starch gives blue colour with iodine?

(ii) Which polysaccharide acts as structural material in plants?

(iii) Explain why cellulose does not give blue colour with iodine solution.

Ans :

(i) Amylose.

(ii) Cellulose.

(iii) Amylose possesses helical structure capable of trapping iodine molecules forming blue coloured complex. Cellulose contains straight fibrous chains with extensive hydrogen bonding and lacks helical arrangement. Therefore iodine molecules cannot become trapped and cellulose does not show blue colour.

165. A biology student compared starch and cellulose present in plants. It was observed that starch could be digested by humans whereas cellulose passed undigested through the alimentary canal. The teacher related this difference to the nature of glycosidic linkages present in the two polysaccharides.

(i) Which type of linkage is present in starch?

(ii) Which enzyme required for cellulose digestion is absent in humans?

(iii) Explain why cellulose cannot be digested by humans.

Ans :

(i) α-glycosidic linkage.

(ii) Cellulase.

(iii) Cellulose contains β-glycosidic linkages between glucose units. Human digestive system lacks cellulase enzyme required for hydrolysis of these bonds. Therefore cellulose cannot be digested although starch containing α-glycosidic bonds is easily hydrolysed.

166. A student dissolved glycine in water and passed electric current through the solution. At a particular pH, glycine did not migrate towards either electrode. The teacher explained that amino acids behave differently at different pH values because they exist as zwitter ions in aqueous medium.

(i) What is the ionic form of amino acids in aqueous solution called?

(ii) What is the pH at which amino acid does not migrate in electric field called?

(iii) Explain why amino acids show amphoteric behaviour.

Ans :

(i) Zwitter ion.

(ii) Isoelectric point.

(iii) Amino acids contain both acidic carboxyl group and basic amino group.

$^{+}NH_3CH(R)COO^{-}$

They can donate proton through carboxyl group and accept proton through amino group. Therefore amino acids react with both acids and bases and behave as amphoteric compounds.

167. During a practical demonstration, egg albumin was heated strongly and its texture changed permanently. The teacher explained that heating destroys the higher structural organisation of proteins responsible for biological activity.

(i) Name the process responsible for this change.

(ii) Which structure of protein remains unaffected during this process?

(iii) Explain how heating affects protein structure.

Ans :

(i) Denaturation.

(ii) Primary structure.

(iii) Heating disrupts hydrogen bonds and weak intermolecular forces responsible for secondary and tertiary structures of proteins. As a result proteins lose their specific three-dimensional shape and biological activity. However peptide bonds remain intact and therefore primary structure remains unchanged.

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135. Explain why proteins get denatured on heating whereas carbohydrates generally do not show such behaviour.

ISC 2011

Ans :

Proteins possess complex secondary and tertiary structures stabilised by weak hydrogen bonds and intermolecular forces.

Heating disrupts these weak interactions causing denaturation.

Carbohydrates do not possess such highly organised three-dimensional structures and therefore generally do not undergo denaturation on heating.

136. During DNA replication, each parental strand acts as template for synthesis of a new strand. Explain how complementary base pairing ensures accuracy during this process.

ISC 2022

Ans :

Complementary base pairing occurs specifically as:

$A - T$

$G - C$

During replication each parental strand directs formation of complementary strand using these pairing rules.

This specific pairing ensures exact duplication of genetic information and maintains hereditary continuity.

137. A student found that glucose gives positive Fehling's test while sucrose does not. Explain the structural basis for this difference.

ISC 2019,

Ans :

Glucose contains free aldehydic group in open chain form which reduces Fehling's solution producing red precipitate of cuprous oxide.

In sucrose, the reactive aldehydic and ketonic groups are involved in glycosidic bond formation and remain unavailable for reduction.

Therefore sucrose gives negative Fehling's test.

138. What is denaturation of proteins?

ISC 2023

Ans :

A change in physical and biological properties of a protein without affecting its chemical composition is called denaturation of protein. It may be affected by the action of heat, alcohol, acid, radiation etc. Denaturation changes only the secondary and tertiary structures of protein, the primary structure remains unchanged. This process is irreversible in most cases. However, in some cases, it may be reversed and is termed as renaturation. Coagulation of egg and curdling of milk are common example of denaturation of proteins.

139. A student hydrolysed maltose and obtained only one type of monosaccharide. However, sucrose on hydrolysis produced two different monosaccharides. Identify the monosaccharides obtained from both carbohydrates and explain why sucrose behaves as a non-reducing sugar.

ISC 2023, 2011

Ans :

Maltose on hydrolysis gives two molecules of glucose.

Sucrose on hydrolysis gives:

1. Glucose
2. Fructose

Sucrose behaves as a non-reducing sugar because the anomeric carbon atoms of both glucose and fructose are involved in glycosidic bond formation. Therefore no free aldehydic or ketonic group remains available for reduction reactions.

NODIA

140. A student compared amylose and amylopectin present in starch. Differentiate between them on the basis of structure and iodine test.

ISC 2017, 2012

Ans :

Amylose	**Amylopectin**
Linear polymer of glucose.	Branched polymer of glucose.
Gives blue colour with iodine.	Does not give blue colour with iodine.

Amylose possesses helical structure while amylop ectin contains branched chains.

141. What is glycogen? How is it different from starch?

ISC 2005

Ans :

Glycogen is a highly chain condensation polymer of α-D-glucose. It is stored in the form of glucose in liver and muscles of human beings.

In contrast, starch is a chief storage polysaccharide of plants and consists of a mixture of two components, amylose (water soluble

Ans :

(i) Amylopectin.

(ii) Amylose.

(iii)

Amylose	**Amylopectin**
Linear helical polymer.	Branched polymer.
Contains mainly α-1,4-glycosidic linkages.	Contains α-1,4 and α-1,6-glycosidic linkages.

Amylose gives blue colour with iodine whereas amylopectin does not give deep blue colour.

****

NODIA

168. A student studied DNA replication using a model showing complementary base pairing between nitrogenous bases. The teacher explained that accurate pairing of bases ensures faithful transmission of genetic information from one generation to another.

(i) Which base pairs with adenine in DNA?
(ii) Which base pairs with guanine in DNA?
(iii) Explain the importance of complementary base pairing during replication.

Ans :

(i) Thymine.
(ii) Cytosine.
(iii) During replication each parental DNA strand acts as template for synthesis of complementary strand. Specific pairing:
$A - T$
$G - C$
ensures exact duplication of genetic information and maintains hereditary continuity during cell division.

169. A biochemistry student studied the hydrolysis of proteins in acidic medium and observed formation of simpler organic compounds. The teacher explained that proteins are polymers formed from amino acids linked through peptide bonds.

(i) Which bond links amino acids in proteins?
(ii) What are the final products obtained after complete hydrolysis of proteins?
(iii) Explain how peptide bonds are formed between amino acids.

Ans :

(i) Peptide bond.
(ii) Amino acids.
(iii) Peptide bond is formed by condensation between amino group of one amino acid and carboxyl group of another amino acid with elimination of water molecule.

$$-\mathrm{COOH} + -\mathrm{NH_2} \rightarrow -\mathrm{CO} - \mathrm{NH} - + \mathrm{H_2O}$$

Repeated formation of peptide bonds produces proteins.

170. A student compared globular proteins and fibrous proteins present in the human body. It was observed that enzymes dissolved easily in water whereas keratin remained insoluble. The teacher explained that protein structure determines its physical properties and biological role.

(i) Which category of proteins includes enzymes?
(ii) Name one fibrous protein present in human body.
(iii) Differentiate between globular and fibrous proteins on the basis of structure and solubility.

Ans :

(i) Globular proteins.
(ii) Keratin.
(iii)

Globular Proteins	**Fibrous Proteins**
Compact spherical structure.	Long thread-like structure.
Soluble in water.	Insoluble in water.

Globular proteins mainly perform functional roles whereas fibrous proteins mainly provide structural support.

171. During a laboratory experiment, a student prepared separate solutions of glucose and fructose. Both solutions reduced Fehling's solution although fructose is a ketose sugar. The teacher explained that fructose undergoes structural transformation under alkaline conditions.

(i) Which functional group is present in fructose?
(ii) Which reagent is reduced in Fehling's test?
(iii) Explain why fructose gives positive Fehling's test.

Ans :

(i) Ketonic group.
(ii) Cupric ions.
(iii) In alkaline medium of Fehling's solution, fructose undergoes tautomerisation forming glucose and mannose which contain aldehydic groups. These aldehydic forms reduce cupric ions to cuprous oxide. Therefore fructose behaves as a reducing sugar despite being a ketose.

172. A student studied the structures of amylose and amylopectin present in starch. It was found that one component possessed branched structure while the other possessed linear helical structure responsible for iodine test.

(i) Which component of starch possesses branched structure?
(ii) Which component gives blue colour with iodine solution?
(iii) Differentiate between amylose and amylopectin on the basis of structure.

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